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Documentation for the Gridded Hourly Atrazine Emissions Data Set for the Lake Michigan Mass Balance Study

A Final Contract Report

by

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Summary

In order to develop effective strategies for toxics management, the Great Lakes National Program Office (GLNPO) of the United States Environmental Protection Agency (U.S. EPA), in 1994, launched an ambitious five year program to conduct a mass balance study of selected toxic pollutants in Lake Michigan for the target year of 1995 (U.S. EPA, 1998). Three persistent organic pollutants (POPs) and one heavy metal have been selected for the focus of the Lake Michigan Mass Balance (LMMB) study: polychlorinated biphenyls (PCBs), trans-nonachlor, atrazine and mercury.

Atrazine is a broadleaf herbicide typically applied to corn, sorghum, sugarcane, pastures, sweet corn, seed crops and sod (Gianessi and Puffer, 1991). In 1991, applications to corn and sorghum accounted for approximately 95% of the total atrazine usage in the United States (Gianessi and Puffer, 1991). Atrazine is typically applied as a pre-emergent spray and/or a post-emergent spray although it can also be incorporated into the soil prior to planting (USDA, 1995a). Peer reviewed literature suggests that atmospheric sources of atrazine may be an important input of herbicide to the Lake Michigan system (Schottler and Eisenreich, 1997). The National Oceanic and Atmospheric Administration (NOAA) is collaborating with the LMMB study in its estimation of the atmospheric deposition of atrazine to Lake Michigan.

The modeling of atrazine deposition to Lake Michigan has three essential components - the emission of atrazine following its application, transport by the atmosphere and wet and dry removal from the atmosphere to the lake. Under an interagency agreement between NOAA and the U.S. EPA, NOAA contracted with Canadian ORTECH Environmental to generate an hourly atrazine emissions data set for the period April 1, 1995 - July 16, 1995 using Canadian ORTECH Environmental's Pesticide Emission Model (PEM) (Scholtz *et al.*, 1997). The episodic atrazine inventory generated by PEM will be input to the U.S. EPA Community Multiscale Air Quality (CMAQ) model of atmospheric transportation, transformation and deposition (Byun and Ching, 1999). Results of the linked PEM/MM5-PX/CMAQ system will then be provided to the in-lake fate and transport model MICHTOX (Rygwelski, *et al.*, 1999). This enhanced information should, in turn, improve the ability of the U.S. EPA to evaluate, *via* tools such as MICHTOX, the effect of atrazine use management decisions on atmospheric loadings of atrazine to Lake Michigan.

Canadian ORTECH Environmental has completed the emissions data generation and this report documents only those aspects of the modeling of the atrazine emissions that are specific to the LMMB study. A complete description of the physics and underlying assumptions inherent in PEM can be found in Scholtz *et al.* (1997). PEM is a numerical model that solves for the vertical advection and diffusion of heat, moisture and pesticide concentration in agricultural soils in either the absence or presence of a crop canopy; horizontal diffusion and advection are neglected. At the soil surface, PEM is coupled to the atmospheric surface layer through a surface energy balance, with the sensible and latent heat fluxes in the atmospheric surface layer being modeled using similarity theory (Businger *et al.*, 1971). PEM also includes a modified "big leaf" canopy sub-model (Hicks *et al.*, 1987) which

accounts for spray interception by the vegetation canopy as well as the subsequent volatilization and/or wash off during precipitation events.

PEM supports three different modes of pesticide application; application on treated seed, pre- and post-emergent spraying, and incorporation into the soil. For the LMMB study, atrazine is assumed to be applied as a pre-emergent spray and/or an early growing season post-emergent spray. For each grid cell, PEM required the following constant parameters: the predominant soil texture, the total atrazine applied (kg/grid), the date of the first atrazine application and the amount applied, and the date of the second atrazine application and the amount applied (if any). NOAA provided these data to Canadian ORTECH Environmental for input to the PEM. In the United States, the application periods were assigned based on state-level USDA Weekly Crop Progress Reports for 1995 (USDA, 1995b). In Canada, application dates were based on long-term average planting date statistics. Gridded 1995 atrazine usage for the United States was estimated from data provided by the U.S. Geological Survey Pesticide National Synthesis Project (U.S. Geological Survey, 1998), while usage data for Canada were supplied to NOAA by Environment Canada. Heaviest atrazine usage is centered around the corn belt states which are located to the south and southwest of Lake Michigan. Isolated pockets of high usage also occur in Maryland and in Pennsylvania.

The CMAQ fate and transport model will be explicitly linked with the PEM through the hourly emissions inventory and meteorological conditions. CMAQ is driven by the Fifth Generation Pennsylvania State University/National Center for Atmospheric Research (NCAR) Mesoscale Meteorological model (MM5), coupled to a land-surface model (MM5-PX) (Pleim and Xiu, 1995). In order that the atrazine emissions modeled by PEM be consistent with the meteorology used by CMAQ, PEM was modified to accept the meteorological information required for the estimation of atrazine volatilization from the MM5-PX .

Both the MM5-PX and PEM include models of the heat and moisture processes in the soil. The MM5-PX model deals with processes on spatial scales that are consistent with its modeling grid interval, which may include several landuse types. The PEM, however, simulates volatilization on the scale of a crop field. An important aspect of the emissions modeling presently reported is a methodology that was developed to make the PEM atrazine emission predictions consistent with the meteorology provided by the MM5-PX model. This involved modifying some of the parameterizations in the PEM to agree with those of the MM5-PX. In the course of quality assurance runs with PEM, any anomalous results were investigated and rectified. Most anomalies were traced to conflicts arising from treatment of snow cover and grids that included both water and cropland. Also, as part of the quality assurance, the surface soil temperatures and moistures predicted by PEM and by the MM5-PX model were compared. In general, the agreement between the predicted surface soil temperatures and soil moisture from the two models was very good.

In order to assess the behavior of the PEM in predicting atrazine emissions, the emissions from several grid cells were examined in detail by comparing the patterns of emission with the occurrence of precipitation events and prolonged periods of drying of the soil. Precipitation tends to suppress atrazine emission by leaching the pesticide away from the soil surface, while drying of the soil leads to an accumulation of atrazine at the soil surface and

an increasing volatilization rate. In all of the grid cells examined, the behavior of PEM was fully consistent with expectations based on the model physics and the results of other studies. As a final quality assurance step, animated visualizations for the entire study domain were made of the gridded emission fields, temperature and moisture fields, and other parameters. The diurnal cycling of the atrazine emissions (which may cover some two orders of magnitude) and the impacts of precipitation and soil drying events are clearly evident in these animations.

This study has demonstrated that the PEM can be integrated for an extended period (106 days) without reinitializing the soil moisture and temperature profiles; this indicates that the modeled balance between evapotranspiration, precipitation and drainage from the soil, over the period simulated, is reasonable. It has also demonstrated that the PEM model can be successfully coupled *via* a one-way linkage with the MM5-PX model to form the first half of the PEM/MM5-PX/CMAQ linked assessment system.

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1. Introduction

In order to develop effective strategies for toxics management, the Great Lakes National Program Office (GLNPO) of the United States Environmental Protection Agency (U.S. EPA), in 1994, launched an ambitious five year program to conduct a mass balance study on Lake Michigan for the target year of 1995 (U.S. EPA, 1998). The mass balance concept, essentially, involves the principle of mass conservation, whereby the mass of pollutant entering the lake equals the amount exiting plus any amount stored or chemically altered in the lake. Determining the pollutant loadings associated with the atmosphere, rivers and tributaries as well as understanding how the pollutants are transported through the lake and its foodweb are critical parameters.

Three persistent organic pollutants (POPs) and one heavy metal have been selected for the focus of the Lake Michigan Mass Balance (LMMB) study: polychlorinated biphenyls (PCBs), trans-nonachlor, atrazine and mercury. Each of these pollutants represent a class of pollutants. For example, mercury is a toxic, bioaccumulative and persistent metal that is emitted from a wide variety of industrial and natural sources. Atrazine was chosen to represent triazine herbicides, a class of current, widely used agricultural chemicals. Although atrazine does not currently appear on the U.S. EPA Great Waters Pollutants of Concern list, it is included on the Chesapeake Bay Toxics of Concern list and is currently under evaluation for addition to the Great Waters list (U.S. EPA, 1997).

Atrazine is a broadleaf herbicide typically applied to corn, sorghum, sugarcane, pastures, sweet corn, seed crops and sod (Gianessi and Puffer, 1991). In 1991, applications to corn and sorghum accounted for approximately 95% of the total atrazine usage in the United States (Gianessi and Puffer, 1991). For simplicity, the LMMB study only considers the atrazine emissions from corn and sorghum. Atrazine is typically applied to the field as a pre-emergent spray and/or a post-emergent spray, although it can also be incorporated into the soil prior to planting (USDA, 1995a).

Preliminary results of tributary and observation-based loadings estimates show that about 25% of atrazine inputs to Lake Michigan are from the atmosphere. The remaining 75% are from tributary inputs that bring atrazine laden run-off to the lake (Schottler and Eisenreich, 1997). Therefore, atmospheric sources of atrazine appear to be an important input of herbicide to the Lake Michigan system.

In order to estimate the atmospheric loadings of atrazine to Lake Michigan, an understanding of how atrazine is first emitted to the atmosphere from agricultural crops and soils following application is required. Experimentally measured atrazine emissions from crop lands to the atmosphere indicate that the volatilization flux can vary markedly over a diurnal cycle, and that they are strongly influenced by the local soil and meteorological conditions (Glottfelty *et al.*, 1989). The LMMB study has adopted a modeling approach whereby the hourly atrazine emissions are estimated using the Pesticide Emission Model (PEM) (Scholtz *et al.*, 1997), which is driven by meteorological data generated by the Fifth Generation Pennsylvania State University/National Center for Atmospheric Research (NCAR) Mesoscale Meteorological model (MM5), coupled to a land-surface model (MM5-PX) (Pleim and Xiu, 1995). The

episodic atmospheric atrazine inventory generated by PEM, as well as MM5-PX generated meteorological fields such as temperature, humidity, wind speed and wind direction will be passed to the U.S. EPA Community Multiscale Air Quality (CMAQ) model (Byun and Ching, 1999), an atmospheric transportation, transformation and deposition model. CMAQ, in turn, will predict the air concentrations of atrazine above Lake Michigan as well as the wet and dry deposition loadings to the lake. Finally, meteorological state, and wet and dry atmospheric deposition loads at the lake surface will be passed to MICHTOX (Rygwelski *et al.*, 1999), an unsteady-state, Water Quality Simulation Program (WASP) model. Results generated by this linked modeling system should improve the ability of the U.S. EPA to reasonably evaluate the impact of past, present or future chemical management decisions on atrazine loadings to Lake Michigan.

This report details the methodology used to generate hourly atrazine emissions from agricultural lands using PEM for the LMMB study. In addition, this report also describes modifications to PEM in order to make PEM and the soil model contained within the MM5-PX model consistent. A complete description of the physics and underlying assumptions inherent in PEM can be found in Scholtz *et al.* (1997).

2. Overview Of PEM and Required Inputs

2.1 Overview of PEM

As mentioned above, the complete details of PEM can be found in Scholtz *et al.* (1997). A brief overview of the model, however, is provided in this section to familiarize readers with the essential details of PEM. Readers requiring a deeper understanding of the model are encouraged to review Scholtz *et al.* (1997).

PEM is a numerical model created to solve for the vertical advection and diffusion of heat, moisture and pesticide concentration in agricultural soils in either the absence or presence of a crop canopy. The model is driven by hourly meteorological data available from climate observing stations or from a meteorological model. Horizontal diffusion and advection are neglected within the upper one meter of the soil column which has been divided into 45 variable spaced levels, with the greatest resolution approaching the soil surface. The relatively large number of levels in PEM is required to properly define the pesticide concentration profile in the soil near the surface for computing the volatilization rate. The time dependent, one-dimensional governing equations for heat, moisture and pesticide concentration are solved using finite element techniques with a time step of 1200 seconds.

At the soil surface, PEM is coupled to the atmospheric surface layer through a surface energy balance. The sensible and latent heat fluxes are modeled using similarity theory (Businger *et al.*, 1971) for the atmospheric surface layer, while the radiative heat fluxes are modeled using a simple radiation model which employs the incoming solar radiation at the ground surface (Munn, 1966). Soil moisture and heat fluxes are determined by PEM. A comparison of modeled and measured volatilization fluxes from bare soils for spray applied triallate and trifluralin has been conducted (Scholtz *et al.*, 1994, and Scholtz *et al.*, 1997) and shows good agreement between the field data and model estimates over a five day period following the pesticide application.

PEM is also coupled to a modified “big leaf” canopy sub-model (Hicks *et al.*, 1987) which accounts for spray interception by the vegetation canopy as well as the subsequent volatilization and/or wash off during precipitation events. A suitable field data set has not been found against which to evaluate the canopy sub-model. A sensitivity analysis, however, indicates that the canopy sub-model estimates generally lie within the broad range of the sparse data available in the literature.

PEM supports three different modes of pesticide application. In the seed treated mode, the pesticide is applied at the time of planting in the form of treated seed or in-furrow application centered at a depth of 7 cm. This mode effectively buries the pesticide beneath the soil surface with little pesticide exposed to the atmosphere. The soil incorporated mode involves the application of the pesticide at the time of tilling during the preparation of the soil for planting. In this mode, it is assumed that the pesticide is uniformly mixed in the upper 10 cm of the soil column. In the spray applied mode, the pesticide is applied to the soil and/or canopy surface in the form of a spray or dust. There is little penetration of the pesticide into the soil column (assumed to be all within the upper 1 cm) and the applied pesticide is immediately exposed to the atmosphere. PEM allows for four different timings associated with the spray application: a pre-emergent spray, an early growing season post-emergent spray, a mid-growing season post-emergent spray and a late growing season post-emergent spray. In the case of the post-emergent sprays, part of the applied pesticide will impinge on the crop canopy. For the LMMB study, atrazine is assumed to be applied as a pre-emergent spray and or an early growing season post-emergent spray. Details of the application dates are given below in the section detailing the constant grid cell data.

2.2 PEM Input Requirements

The domain of the study, which is identical to that used by the MM5-PX and CMAQ models, covers the eastern two thirds of the United States as well as the southern parts of the central and eastern Canadian provinces. There are over 7000 grid cells in the domain with each grid cell being approximately 36 km by 36 km. The time frame of interest is from April 1995 through to July 1995.

For each grid cell in the domain, PEM requires, as inputs, hourly meteorological data, geophysical data, soil properties, and the physical/chemical properties of atrazine. The hourly meteorological data, discussed in detail below, are provided by the National Oceanic and Atmospheric Administration (NOAA) using the MM5-PX model. The geophysical data are provided in the form of a grid constant file provided by NOAA which gives specific information for each grid cell in the domain. Details of the grid constant file are also discussed below (Section 2.2.2).

The soil texture scheme used by PEM is that of Clapp and Hornberger (1978). Inputs required by PEM include field capacity, saturation capacity, wilt point, saturation hydraulic conductivity, soil constant and saturation matric potential. These parameters are given in Table 2.1 for the twelve Clapp and Hornberger (1978) soil textures.

The physical/chemical properties of atrazine used by PEM are as follows:

diffusivity in air = $0.498 \text{ m}^2/\text{day}$ (estimated using Sherwood *et al.*, 1975)
 diffusivity in water = $0.466 \times 10^{-4} \text{ m}^2/\text{day}$ (estimated using Sherwood *et al.*, 1975)
 organic carbon sorption coefficient, $K_{oc} = 0.100 \text{ m}^3/\text{day}$ (Wauchope *et al.*, 1992)
 Henry's Law coefficient, $K_H = 1.19 \times 10^{-7} (\text{kg}/\text{m}^3)/(\text{kg}/\text{m}^3)$ (Suntio *et al.*, 1988)
 solubility = $1.07 \text{ kg}/\text{m}^3$ (Suntio *et al.*, 1988)
 half-life in the soil = 90 days (Wauchope *et al.*, 1992)

2.2.1 Hourly Inputs to PEM from MM5-PX Model Output

The hourly meteorological data required to drive the development of the soil profiles for heat, moisture and atrazine concentration in PEM are obtained from the MM5-PX model outputs. Required variables include: the year, month, day and hour of the record, the reference height, z_{ref} , the surface u and v wind components at z_{ref} , the mixing ratio at z_{ref} , the air temperature at z_{ref} , the reference surface pressure, precipitation rate (sum of both convective and non-convective), the emissivity, the solar radiation at the surface, and the aerodynamic conductance. In addition, at the start of the simulation, PEM also requires the MM5-PX surface soil layer and deep soil layer temperature and moisture to initialize the profiles in PEM.

The MM5-PX model outputs have been provided by NOAA spanning the simulation period from April 01 to July 16, 1995 in five data files given by:

<u>Data File Name</u>	<u>Coverage Period</u>
apr1_23.dat	April 01 to April 23, 1995
apr23_may16.dat	April 23 to May 16, 1995
may16_jun7.dat	May 16 to June 07, 1995
jun7_30.dat	June 07 to June 30, 1995
jun30_jly16.dat	June 30 to July 16, 1995

2.2.2 Constant Grid Cell Data

For each grid cell, PEM requires the following constant parameters: latitude and longitude coordinates of the centroid of the grid cell, the predominant soil texture within a grid cell, the total atrazine applied (kg/grid) to the grid cell, the date of the first atrazine application with the percentage applied, and the date of the second atrazine application (if any) with the percentage applied.

Predominant soil texture for each PEM and MM5-PX grid was estimated for U.S. cells from the State Soil Geographic Database (STATSGO) (USDA, 1994) and for cells in Canada from the Food and Agricultural Organization (FAO) Soils Map of the World (Zobler, 1986). Soil Characteristics associated with each texture type are taken from Clapp and Hornberger (1978). A plot of the gridded soil texture values is given in Figure 2.1.

The mode and timing of an atrazine application vary with crop (corn or sorghum) and soil texture. For instance, in the Southeastern United States, atrazine is evenly divided between pre-emergent and early post-emergent applications (USDA, 1995a). In the Upper Mid-West and Plains states, pre-emergent applications dominate (USDA, 1995a). It is assumed that there are no more than two periods of atrazine application in a LMMB grid cell. Two periods

are assigned only if both corn and sorghum are planted in the region, or if on-going field activities are significantly interrupted by unfavorable weather conditions (a frequent occurrence in 1995). In the United States, the application periods were assigned based on state-level USDA Weekly Crop Progress Reports for 1995 (USDA, 1995b). In Canada, application dates were based on long-term average planting date statistics. First and second application dates for the study domain are given in Figures 2.2 and 2.3 respectively. The application dates correspond to the 14th day of a 21 day application period.

Gridded 1995 atrazine usage for the United States was estimated from data provided by the U.S. Geological Survey Pesticide National Synthesis Project (U.S. Geological Survey, 1998). Usage data for Canada has been supplied to NOAA by Y.F. Li of Environment Canada (Personnel Communication). The combined atrazine usage data set is given in Figure 2.4. Heaviest atrazine usage is centered around the corn belt states which are located to the south and southwest of Lake Michigan. Isolated pockets of high usage also occur in Maryland and in Pennsylvania.

3. Pesticide Emission Model Modifications

3.1 Initial Compatibility Modifications to PEM

In order to make PEM more consistent with the MM5-PX model, initial modifications to the logic and physics of PEM were implemented and are detailed below.

3.1.1 Conversion to an Episodic Model

The original pesticide emission model was developed to run for three years of repeated yearly meteorological data as obtained from climate stations located in the domain of interest. The original model was set up to calculate the volatilization fluxes for a given station for the entire period of the simulation before moving on to the next meteorological station. Gridded weekly and seasonal emissions were calculated from the model output in a separate database which linked the grids cells of the domain to the various climate stations. Figure 3.1 gives a schematic of the program logic of the original pesticide emission model.

The logic of the pesticide emission model has been modified to create an episodic version of the code which employs the modeled meteorological data generated by the MM5-PX for each grid cell in the domain of interest. The code is executed in such a way that hourly emissions are calculated for all grids at each time step before proceeding to the next time step. The database post-processing of the previous model is now incorporated directly into the episodic version of the code. Figure 3.2 illustrates the logic schematic of the new episodic pesticide emissions model.

3.1.2 Evaporation from Bare Soil

The modeled evaporation from the bare soil in PEM has been modified by incorporating a β correction term in the soil surface evaporation rate, E_o [kg/(m²s)], given by (Ye and Pielke, 1993 and Lee and Pielke, 1992):

$$E_o = \rho_a \beta \frac{q_{sat}(T_o) - q_a}{r_a} \quad (3.1)$$

where ρ_a [kg/m³] is the air density, q_{sat} [kg water vapor/kg air] is the specific humidity at the saturation condition, q_a [kg water vapor/kg air] is the specific humidity of the air, T_o [K] is the soil surface temperature, and r_a [s/m] is the resistance associated with the turbulent transport water vapor in air. β [dimensionless] has the functional form:

$$\beta = \begin{cases} 0.25 \left[1 - \cos \left(\frac{\pi \theta}{\theta_{fc}} \right) \right]^2, & \text{if } \theta < \theta_{fc} \\ 1.0, & \text{if } \theta \geq \theta_{fc} \end{cases} \quad (3.2)$$

and where θ [volumetric fraction] is the moisture of the soil and θ_{fc} [volumetric fraction] is the field capacity of the soil.

The above technique for limiting the evaporation rate from drying bare soil takes into account the moisture conditions in the soil matrix. In the original pesticide emission model, the method of calculating the evaporation from the bare soil assumed that the soil moisture could not drop below the air dry soil moisture level ($\theta_{air\ dry}=0.1$).

The inclusion of the β correction term in PEM makes the estimation of the evaporation from bare soil consistent with that of the MM5-PX model.

3.1.3 Henry's Law Temperature Correction

The original pesticide emission model used a temperature correction for the Henry's Law coefficient (air-water partition coefficient) by assuming that the temperature dependency of the coefficient for atrazine was similar and scaleable with that of the pesticide lindane. For the Lake Michigan Mass Balance study, the temperature dependency for atrazine is given by:

$$\log(K_H(T)) = \log(K_H(T_{ref})) + \frac{-\Delta H}{2.303R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \quad (3.3)$$

where $K_H(T)$ [(kg/m³)/(kg/m³)] is the Henry's Law coefficient at temperature, T [K], $K_H(T_{ref})$ [(kg/m³)/(kg/m³)] is the Henry's Law coefficient at the reference temperature ($T_{ref}=298.16$ K),

ΔH [kJ/mol] is the enthalpy of volatilization for atrazine taken at 50 kJ/mol (Hornbuckle, 1998) and R [kJ/mol/K] is the universal gas constant.

3.1.4 Distributed Atrazine Application over an Extended Period

Originally, PEM applied all of the pesticide, for a given application mode, in a specific hour of the application day. PEM has been modified to allow for application of a pesticide over an extended period of time with either a uniform or normalized Gaussian distribution. Examples of the two distributions are given in Figure 3.3. In addition, if precipitation is present at the scheduled application time, the model will skip the rain day and proceed with the distribution on the subsequent dry day. For the atrazine study, an application period of three weeks (21 days) and a uniform distribution have been selected.

3.1.5 Soil Properties

The Clapp and Hornberger (1978) soil texture classification scheme has been used. Soil properties for the various texture classifications are given in Table 2.1. Values for the saturation capacity, θ_s , saturation hydraulic conductivity, k_s , the soil constant, b , and the saturation matrix potential, ψ_s , are taken from Clapp and Hornberger (1978) and are identical to those given in Scholtz *et al* (1997). Values for the field capacity, θ_{fc} , and wilt point, θ_w , are taken from Lee and Pielke (1992) and differ from Scholtz *et al* (1997). The field capacity and wilt point moistures from Lee and Pielke (1992) are consistent with the β -correction for the evaporation from bare soil as discussed previously and are also consistent with the values currently used in the MM5-PX model.

In addition, since the MM5-PX soil type #5, described as “silt,” is not a Clapp and Hornberger (1978) soil type, it has been assigned the same properties as that of “silt loam” (MM5-PX soil type #4).

3.2 Additional Pesticide Emission Model Modifications

During the course of early quality assurance runs with PEM, additional difficulties were encountered that warranted further investigation. This section of the report briefly details the difficulties encountered as well as the course of action followed to resolve the issue or limit its sphere of influence.

3.2.1 MM5-PX Snow Cover Event

During a snow cover event, the MM5-PX model assumes that the maximum soil temperature is 0°C and that the surface moisture is at the saturation value for the entire 4.5 days of the MM5-PX simulation. PEM does not consider snow cover and thus cannot simulate these periods in a similar manner as the MM5-PX model. These snow cover events, however, typically occur only in the very early part of the growing season thus providing sufficient time prior to crop planting for PEM to smooth out any perturbations in the soil temperature and moisture profiles resulting from the MM5-PX snow cover event.

3.2.2 MM5-PX Coastal Grid Cells

In coastal cells that contain some land but are predominantly water, the MM5-PX model classifies the soil type as “water.” However, if atrazine is applied to the land portion of the grid cell, the grid constant file classifies the cell as being land having some non-zero atrazine

application. PEM is activated for any cell that has atrazine applications. For a water cell, the MM5-PX model sets the surface layer and deep soil layer moistures to the $wg=w2=0$ respectively which results in a division by zero in the initialization of PEM. As a method around this issue, PEM re-initializes the soil moisture to 75% of the saturation value for the soil type defined in the grid constant file. In addition, PEM assumes a uniform soil temperature profile that is set to the MM5-PX surface water temperature since no representative land temperatures are given for the grid cell.

3.2.3 MM5-PX Solar Radiation versus Net Radiation

PEM has the flexibility to employ either the incoming solar radiation or the net radiation at the surface in its surface energy balance. The sensitivity of the surface energy balance in PEM was tested with both the MM5-PX solar radiation at the surface and the MM5-PX net radiation. It was found that when PEM used the MM5-PX solar radiation at the surface, the predicted soil temperatures at 1 cm were consistently in good agreement with the MM5-PX values except during snow cover events. The MM5-PX solar radiation at the surface was thus selected for use in the surface energy balance of PEM to ensure consistency between the two models.

3.2.4 Definition of Precipitation in the MM5-PX Output

The original units for precipitation in the MM5-PX output were specified as centimeters per hour. It became apparent later in the study that the MM5-PX output is an accumulated precipitation, in meters, over a 4.5 day MM5-PX run. PEM was modified to correctly convert the MM5-PX precipitation values.

3.2.5 Maximum Soil Depth

The maximum soil depth in PEM was modified from a depth of 2 m to a depth of 1 m to be consistent with the maximum depth of the MM5-PX model. In the process, the number of layers in PEM decreased from 49 to 45. Sensitivity runs of PEM did not indicate any significant differences in the prediction of the surface volatilization by changing the depth of the soil column.

3.2.6 Initialization of Soil Temperature and Moisture Profiles in PEM

At the start of the simulation, only the initial values of the MM5-PX surface layer and deep soil layer temperatures (variables tga and $t2$) and moistures (variables wg and $w2$) are used by PEM. For the initialization, the soil column is divided into two zones which span from $z=0$ to $z=-0.01$ m and from $z=-0.01$ to $z=-1.0$ m. In the surface layer, both the soil temperature and moisture are assumed to be uniform and set equal to tga and wg variables respectively. In the lower layer, separate interpolation schemes are used for soil temperature and moisture. For the soil temperature, a power law interpolation is used between tga at $z=-0.01$ m and $t2$ at $z=-1.0$ m. A power law profile was selected since it reflects the general shape of measured soil temperature profiles (see, for example, Munn, 1966). For the soil moisture, a simple linear interpolation is used between wg at $z=-0.01$ m and $w2$ at $z=-1.0$ m since no experimental evidence could be located to justify a more complex interpolation scheme.

It should be noted that as the integration of PEM progresses, the effects of any errors in the initialization diminish rapidly.

3.2.7 Lower Boundary Conditions for Soil Temperature and Moisture in PEM

For soil temperature, the lower temperature boundary condition at 1 m in PEM is set equal to the MM5-PX variable t_2 . This constrains PEM to the same deep soil temperature as the MM5-PX model. The same type of lower boundary condition for moisture was not used. Instead, a "drainage flux" boundary condition has been selected. The "drainage flux" boundary condition, defined by the vertical gradient of the hydraulic conductivity at bottom of the soil column, cumulates the effects of gravity drainage at the bottom of the soil column.

3.2.8 Regional Scales versus Local Scales

During early quality assurance runs, a large difference was noted between the surface soil temperatures at 1 cm predicted by the MM5-PX model and by PEM. In some cases, PEM predicted a soil temperature which, when compared to the MM5-PX predictions, was 12 °C higher during the daytime temperature peaks. An example of a grid cell in Texas is given in Figure 3.4. After detailed examination, the source of the discrepancy was found to be in the selection of the surface roughness used in calculating the aerodynamic resistance in the two models. In the MM5-PX model, the surface cover of the entire grid must be taken into account including that of non-agricultural land. The MM5-PX aerodynamic resistance is therefore based on a "regional" scale of roughness and the atmospheric surface layer, windspeed, humidity, and temperature provided to PEM are, therefore, regional averages. Pesticide volatilization however, is dependent on "local" scales of roughness which determine the aerodynamic resistance controlling the volatilization at the field level. To effectively link the two models, PEM was modified such that the MM5-PX "regional" aerodynamic resistance (the inverse of the MM5-PX variable, ra) was used in determining the transport of heat and moisture from the soil and crop canopy to the atmosphere. The "local" aerodynamic resistance, however, is maintained in the calculation of the atrazine volatilization as the appropriate resistance at the field level. The effect on soil surface temperature prediction with PEM using the MM5-PX "regional" scale is given in Figure 3.5 for the same grid cell as that given in Figure 3.4. The agreement between the soil temperatures has improved significantly to the point where the difference between the two models is only one or two degrees.

An exception to the use of the "regional" scale has been made for the MM5-PX water cells that are classified as land cells with atrazine applications by the grid constant file. For these grid cells, the MM5-PX "regional" aerodynamic resistance is based on an atmospheric boundary layer above a water surface. The nature of the atmospheric boundary layer over a water surface is very different from that over a land surface with vegetation. For this reason, the "local" aerodynamic resistance as calculated by PEM is used to determine the transport of heat and moisture as well as atrazine from the soil and crop canopy for these coastal grid cells.

3.2.9 Bare Soil Local Roughness Length

The "local" roughness length used in the atrazine volatilization calculation from bare soils in PEM has been increased from $z_o=0.0003$ m, as given in Scholtz *et al.* (1997) to $z_o=0.01$ m (Pielke, 1984). While $z_o=0.0003$ m is appropriate for snow covered winter conditions, its magnitude is too small for a tilled soil surface bare of vegetation. The "local" roughness

length is still modified through the growing season to reflect the growing crop canopy up to a maximum of $z_o=0.14$ m in the same manner as described in Scholtz *et al.* (1997).

3.2.10 Reference Soil Moisture

In order to be more compatible with the MM5-PX model, the default wilt point and field capacity soil moisture values in PEM have been changed to match those used in the MM5-PX model and are given in Table 2.1. These new wilt point values tend to be greater in magnitude than the PEM default values and can lead to unrealistic values in the calculation of the moisture transported from the roots to the canopy. The moisture taken up by the roots from the soil is determined by the root uptake function, $g(\theta)$ [dimensionless], given by:

$$g(\theta) = \frac{\theta_{avg} - \theta_w}{\theta_R - \theta_w}, \quad \theta_{avg} \leq \theta_R$$

$$g(\theta) = 1, \quad \theta_{avg} > \theta_R$$
(3.4)

where θ_{avg} [volumetric fraction] is the average moisture in a soil layer and θ_R [volumetric fraction] is the reference soil moisture set at a default value of 0.25 (Mahrt *et al.*, 1983). The new wilt point moistures have values greater than 0.25 for some of the clay soils whereas the PEM default values were all below 0.25. To eliminate any unrealistic root uptake, the reference wilt point moisture in PEM has been increased to 0.30, which is greater than all the wilt point values for the different soil types listed in Table 2.1.

3.2.11 Dispersion Coefficient

The volatilization flux of atrazine has been shown by Jury *et al.* (1984) to be dependent on the magnitude of the water flux within the soil column. Modeling the liquid phase concentration of atrazine within the soil column thus becomes very important. In PEM, the effective bulk diffusivity of a pesticide in the liquid phase, D_L [m²/day], is determined by a modified Millington-Quirk model given by:

$$D_L = \left(\frac{a}{\epsilon} \right)^{3.33} D_{L,m} + \lambda \frac{|J_w|}{\theta}$$
(3.5)

where a is the volumetric air fraction in the soil matrix, ϵ is the soil void fraction, $D_{L,m}$ [m²/day] is the molecular diffusivity of the pesticide in the liquid phase, λ is the dispersion coefficient which is an experimental constant characteristic of the soil pores, θ [volumetric fraction] is the soil moisture and J_w [m²/day] is the soil water flux. The first term on the right hand side of equation (3.5) adjusts the molecular diffusivity to reflect the tortuous path that the water must travel in the soil column. The second term on the right hand side is a dispersion correction term. Since the soil is a non-uniform porous medium, the individual

pore water velocities will be different due to the effects of differing pressure differentials and capillary effects. If a liquid phase concentration front is present, the front will not be sharp but rather it will be diffuse due to the differing pore water velocities. The dispersion correction term attempts to account for this phenomenon. The applicability of a dispersion correction term in the transport of species concentration in unsaturated zones has been questioned in the literature although there is “reasonably strong evidence” that it holds provided that the dispersion coefficient is equal to a few centimeters (Van Ommen *et al.*, 1989). Literature values for the dispersion coefficient range from 0.003-0.005 m as reported in Bresler (1973) up to 0.036 m as report by Van Ommen *et al.* (1989) for a land use of corn.

The default value for the dispersion coefficient in PEM is $\lambda=0.003$ m. Although the predicted bare soil emissions from PEM have been evaluated against field data for triallate and trifluralin, these pesticides are not sensitive to the soil water flux (Jury *et al.*, 1984) and thus are not sensitive to the value of the dispersion coefficient.

Ideally, the predicted emissions from PEM should be compared to field data for atrazine in order to optimize the value of the dispersion coefficient. The limited field data available for atrazine in the literature is summarized in Table 3.1. The study by Clendenning *et al.* (1990) has the lowest volatilization values of all the studies. This may be due, in part, to the fact that they initially dissolved the atrazine with acetone to increase the solubility. Soil core samples indicated that atrazine concentrations were detected as far down as one meter following the first week after application suggesting that the atrazine and acetone mixture is more readily transported in the soil column than atrazine alone. This, in turn, would cause a decrease in the surface concentration and thus lower volatilization rates. For this reason, this study will not be used for comparison purposes.

None of the field studies listed in Table 3.1 have sufficient data to accurately conduct a full simulation using PEM. Four of the field studies (Glottfelty *et al.*, 1989, Whang *et al.*, 1993, Wienhold and Gish, 1994, and Rice *et al.*, 1998), however, were conducted in the state of Maryland with three of the studies having an atrazine application in either May or June. The remaining field study (Whang *et al.*, 1993) had an atrazine application in mid-April. It thus becomes apparent that the field studies are fairly tightly clustered geographically as well as temporally.

To test the sensitivity of atrazine volatilization to the magnitude of the dispersion coefficient in PEM, a simple numerical experiment was conducted using an isolated grid cell in the state of Maryland (lat/long: 39.00/-76.87). An application date of May 25 and a silt loam soil type were assumed to correspond to the data reported in Glottfelty *et al.* (1989). In addition, the MM5-PX 1995 meteorological data for the isolated grid cell was used to drive PEM. The magnitude of the dispersion coefficient was varied from a value of 0.003 m (PEM default value) to 0.02 m. The resulting cumulative atrazine emissions over 21, 26, 30 and 35 days are given in Table 3.2. It is readily apparent from the table that a larger dispersion coefficient leads to a decrease in the surface volatilization of atrazine.

It is difficult to directly compare the simulated results in Table 3.2 to the experimental results in Table 3.1 since each experiment and the simulation are subject to different conditions,

especially the meteorological data. A first order comparison indicates, however, that the simulated cumulative volatilization is generally higher than the experimental data, even for the largest value of the dispersion coefficient. A closer examination of the MM5-PX meteorological data during the 35 day simulation period indicates that the average daily temperature is approximately 25 °C with only 20 mm of accumulated precipitation. While this average daily temperature is in line with some of the experiments given in Table 3.1, the MM5-PX 1995 precipitation is very low in comparison.

To determine the effect of precipitation on the atrazine volatilization, the MM5-PX meteorological data was modified so that 40 mm of precipitation occurred in the first 21 days (roughly corresponding to Glotfelty *et al.*, 1989). Note that the solar radiation was not adjusted to compensate for the added precipitation events. For a dispersion coefficient of $\lambda=0.010$ m, the percent cumulative atrazine volatilization after 21, 26, 30 and 35 days is 3.3%, 3.7%, 4.3% and 4.7% respectively. The added precipitation has the effect of reducing atrazine volatilization by transporting a portion of the surface applied atrazine deeper into the soil column.

The above simulation with the added precipitation was repeated but with the soil type changed from silt loam (Glotfelty *et al.*, 1989 and Rice *et al.*, 1998) to sandy loam (Whang *et al.*, 1993, Wienhold and Gish, 1995, and Gish *et al.*, 1995). The percent cumulative atrazine volatilization for $\lambda=0.010$ m after 21, 26, 30 and 35 days is 2.9%, 3.3%, 3.8% and 4.2% respectively.

Given these results and the scatter in the experimental data, it was decided that the dispersion coefficient be assigned a value of $\lambda=0.010$ m until such time that a more detailed experimental data set becomes available with which to refine the estimate of the dispersion coefficient.

4. Results and Discussion

4.1 Surface Soil Temperature and Moisture Comparisons

A comparison of the surface soil temperatures and moistures predicted by PEM and by the MM5-PX model has been conducted. In general, the agreement between the predicted surface soil temperatures from the two models is very good. As an example, Figure 4.1 gives the predicted values of the surface soil temperatures of the two models for a grid cell in Maryland (lat/long: 39.00/-76.87) for the period of Julian day 91 to 114 (April 1-23) with a silt loam soil type. The figure indicates excellent agreement in temperature prediction although the PEM results are typically a degree or two cooler during the diurnal peak temperature.

The agreement between the predicted values of the surface soil moisture is not as good as that for the surface soil temperatures. Figure 4.2 gives the surface soil moisture (1 cm layer) predictions for the same grid cell as above and indicates reasonable agreement. For other grid cells, however, especially for those with soil types with higher hydraulic conductivities and located along the eastern seaboard, the agreement is not as good. Figure 4.3 gives the comparison of the surface soil moistures for a grid cell in Delaware (lat/long: 38.50/-75.68)

with a sandy loam soil for the same period as the Maryland grid cell. In this particular case, the MM5-PX model predicts much higher diurnal peaks in the surface moisture compared to that predicted by PEM. However, note that these peaks occur at night so that the effect of such differences on total pesticide emissions may be negligible. Soil surface temperatures for this grid cell displayed the same level of agreement as the Maryland grid cell. It should be noted that observed meteorological data for 1995 indicate that the spring and summer months were particularly dry along the eastern seaboard (CPC, 1995) indicating that the PEM surface soil moisture may be in better agreement than the MM5-PX model for these very dry conditions.

4.2 Atrazine Emissions from Single Grid Cells

The behavior of the hourly emissions of atrazine can best be illustrated by isolating the emission time series from single grid cells. To illustrate different emission patterns, three grid cells have been selected and are located in Maryland (lat/long: 39.00/-76.87), in northern Missouri (lat/long: 40.46/-92.85), and in northern Iowa (lat/long: 43.41/-94.84).

4.2.1 Maryland Grid Cell (lat/long: 39.00/-76.87)

The Maryland grid cell has only one atrazine application period centered on Julian day 117. A total of 5017.46 kg/grid of atrazine is uniformly applied over the 21 days making up the application period. The soil type is silt loam.

Figure 4.4 gives the hourly atrazine emission time series as predicted by PEM. The figure indicates that there is considerable diurnal cycling in the volatilization flux on most days. The maximum hourly atrazine emission is approximately 0.7 kg/grid. The cumulative emission is given in Figure 4.5 and indicates a fairly linear relationship with time. This near linear behavior is somewhat unexpected since experimental evidence (Glotfelty *et al.*, 1989) suggests that a maximum emission rate occurs shortly after application and tapers off as time progresses. This expected behavior would produce an “S” shaped curve for the cumulative emission plot. Looking at the surface soil moisture given in Figure 4.6, it becomes readily apparent that the surface soil for this grid cell is fairly dry and typically less than 0.15. The spikes in the surface soil moisture correspond to precipitation events, which are given in Figure 4.7. Note that the extended periods of suppressed emission in Figure 4.4, such as that occurring from Julian days 120 to 125, 131 to 136 and 148 to 149, are the result of these precipitation events. Precipitation tends to transport atrazine away from the surface thus limiting exposure to the atmosphere as the negative water flux carries the atrazine deeper into the soil column. The extent of emission suppression is dependent on the strength and duration of a precipitation event.

It is also important to note that, during daytime precipitation events or during heavy overcast conditions, the solar radiation at the surface is usually much lower than that for clear sunny skies. Reducing the solar radiation prevents the soil temperatures from rising to their “clear sky” maximum values (*i.e.* under clear sunny skies) which leads to depressed evaporation rates from the soil and, hence, reduced upwards moisture fluxes. The concentrations of atrazine at the surface thus cannot be replenished as quickly from concentrations located deeper in the soil column as would occur on clear sunny days in adequately moist soils. In addition, reduced soil surface temperatures lead to reduced volatilization rates for atrazine

through the temperature dependency incorporated into the Henry's Law coefficient (as given by equation 3.3).

4.2.2 Northern Missouri Grid Cell (lat/long: 40.46/-92.85)

For the grid cell in northern Missouri, a total of 7529.76 kg/grid of atrazine is applied. During the first application period, centered about Julian day 145, only 12% of the total was applied. During the second application period, centered about Julian day 166, 60% of the total was applied. The remaining 28% of the total was applied outside the two application periods as given in the grid constant file. The predominant soil type for this grid cell is silt clay loam.

The hourly atrazine emissions is given in Figure 4.8 and indicates that very little atrazine volatilization results from the first application period (centered on day 145). During the second application period (centered on day 166), the emissions are much greater and reach an hourly maximum on the order of 2 kg/grid. A strong diurnal cycling in the hourly atrazine emission time series is again observed. The cumulative atrazine emission is given in Figure 4.9 and displays an "S" shaped curve. This behavior is in marked contrast to the grid cell in Maryland where the cumulative emissions produced a near linear curve. To explain why the atrazine behavior in this grid cell is different, it is useful to look at the surface soil moisture as given in Figure 4.10 and the precipitation given in Figure 4.11. Figure 4.10 indicates that the surface soil moisture is much greater for this grid cell than that for the Maryland grid cell. When the peak emissions occur during Julian days 160 to 173, a pronounced period of drying in the surface moisture occurs. This is also corroborated by the precipitation data, which indicates frequent precipitation events prior to Julian day 160, followed by a dry period, corresponding to the peak emissions given in Figure 4.8, in which no precipitation occurs. After Julian day 173, a set of major precipitation events occurs.

This grid cell effectively illustrates the link between atrazine volatilization and soil moisture/precipitation conditions. During a precipitation event, the rainwater transports atrazine deeper into the soil column thus removing it away from the soil surface and suppressing any subsequent atrazine emissions. To reach the surface again, the atrazine must either rely on diffusion processes or, more likely, be transported back to the surface when the soil moisture flux reverses directions as the soil dries out due to prolonged evaporation at the surface without precipitation. Thus the behavior of the hourly atrazine emissions in Figure 4.8 can be explained in terms of the soil moisture flux and is correlated with the occurrence or absence of precipitation events.

Looking back at the Maryland grid cell, the soil, in general, is very dry. The precipitation events, although fairly frequent, are not sufficient in duration to raise the soil moisture content as evidenced by the rapid drop-off in the surface soil moisture content after a precipitation event in Figure 4.6. The level of moisture within the soil thus cannot support an adequate upward moisture flux required to effectively transport atrazine to the soil surface and replenish the surface concentration. The near linear curve of the cumulative emissions suggests that the volatilization process is being limited, possibly by the diffusive rate of atrazine within the air of the soil matrix.

4.2.3 Northern Iowa Grid Cell (lat/long: 43.41/-94.84)

The grid cell in northern Iowa has a total of 24,274.00 kg of atrazine applied. Two application periods, the first centered on Julian day 124 and the second centered on Julian day 145, are modeled to apply 50% and 45% of the pesticide respectively. The predominant soil type in this grid cell is silt.

The hourly atrazine emissions for this grid cell, given in Figure 4.12, indicate multiple peaks in the time series. These peaks, however, do not necessarily correspond to the application periods. For example, during the second 21 day application period, centered on Julian day 145, a major suppression in the emissions occurs between Julian days 147 and 153. In addition, hourly emissions are effectively curtailed after Julian day 172. The maximum hourly emission is approximately 3.5 kg/grid. The cumulative emission is given in Figure 4.13 and displays somewhat of an “S” shaped curve with a plateau in the center corresponding to Julian days 147 to 153. Looking at the surface soil moisture and the precipitation given in Figures 4.14 and 4.15 respectively again shows that peak hourly emissions occur during prolonged soil drying periods following a precipitation event. This corresponds to conditions when adequate soil moisture exists to transport atrazine to the surface and thus replenish the surface concentration that has been depleted by volatilization. The suppressed emissions during Julian days 147 to 153 can be attributed to the prolonged precipitation event on Julian day 146. The curtailed emissions after Julian day 172 are due to frequent precipitation events during Julian days 173 to 178 which result in a persistent downward water flux. This, in turn, elevates the surface soil moisture from a mean of approximately 0.1 to a mean on the order of 0.3 (see Figure 4.14).

4.3 Atrazine Emissions from the Entire Domain

The hourly emissions from the entire domain over the study period are too numerous to present concisely in a report format. Instead, four hourly distributions for the entire domain have been selected to illustrate the general trends in the data. The four distributions are for Julian day 158 (June 7) at times of 07:00 UT (02:00 EST), 14:00 UT (09:00 EST), 19:00 UT (14:00 EST), and 24:00 UT (19:00 EST) and are given in Figures 4.16 through 4.19. The figures show the progression of atrazine emissions during a typical day. During the early morning hours, the emissions are fairly muted due to the cooler night time temperatures (see Figure 4.16). Stronger emissions occur in Nebraska, in the region surrounding southern Lake Michigan, and in the Maryland region, all of which report heavy atrazine usage. As the sun rises, the surface temperatures increase as does the evapotranspiration and the emissions (see Figure 4.17). This is especially notable in the region south of Lake Michigan. Peak mid-day emissions, given in Figure 4.18, are the result of both the temperature effects on the Henry's Law coefficient and the increased soil water flux that carries atrazine to the soil surface. As evening approaches, the emissions are still reasonably strong (see Figure 4.19) due to the solar heating of the surface but eventually taper off as the surface cools. Predicted atrazine emissions on Julian day 158 from the southern states are relatively minor in comparison to those predicted for the region south of Lake Michigan since the atrazine application and its associated peaks in the south occur earlier in the simulation period.

The complete gridded hourly atrazine emission data set, covering the period of April 01 to July 16, 1995 at a 36x36 km² resolution, has been supplied to Dr. Ellen Cooter on CD ROM in flat

ASCII spatial output arrays. A copy of the supplied README.TXT is given in Appendix A. The data set is divided into five data files matching the time periods covered by the MM5-PX meteorological data files and are given by:

<u>Data File Name</u>	<u>Coverage Period</u>
apr1_23.ems.gz	April 01 to April 23, 1995
apr23_may16.ems.gz	April 23 to May 16, 1995
may16_jun7.ems.gz	May 16 to June 07, 1995
jun7_30.ems.gz	June 07 to June30, 1995
jun30_jly16.ems.gz	June 30 to July 16, 1995

CD ROM copies may be obtained by contacting Dr. Ellen Cooter at cooterej@hpcc.epa.gov. An animation of a portion of the data base may be viewed *via* a link provided on the LMMB project Web page: <http://www.epa.gov/glnpo/lmb/>.

5. Conclusions

To assess the behavior of PEM in predicting atrazine emissions, the emissions from several grids have been examined in detail by comparing the pattern of emissions with the occurrence of precipitation events and prolonged periods of soil drying. In all the examined grid cells the behavior of the PEM predictions is fully consistent with expectations based on the model physics and the results of other studies. As a further quality check on the PEM predicted atrazine emissions, animated visualizations for the gridded soil surface temperature, soil surface moisture, and atrazine emissions have been made for the entire study domain. These animations clearly depict the expected effects of precipitation and soil drying as well as the diurnal cycling of atrazine emissions.

It can be concluded, based on the results of this study, that:

- the soil surface temperature and moisture prediction methodologies in PEM and MM5- PX are compatible,
- the PEM predicted atrazine emission estimates over a 36 km square grid cell show reasonable agreement with field measured atrazine emissions, and
- PEM correctly represents geographic variability in the diurnal pattern of hourly atrazine emissions throughout the study domain.

This study has demonstrated that the PEM can be integrated for an extended period (106 days) without reinitializing the soil moisture and temperature profiles; this indicates that the modeled balance between evapotranspiration, precipitation and drainage from the soil, over the period simulated, is reasonable. It has also demonstrated that the PEM model can be successfully coupled *via* a one-way linkage with the MM5-PX model to predict hourly atrazine emissions to form the first half of the PEM/MM5-PX/CMAQ linked system. Results (atmospheric state, wet and dry atrazine deposition) of the PEM/MM5-PX/CMAQ system will, eventually, be provided to the in-lake fate and transport model MICHTOX (Rygwelski, *et al.*, 1999). This model-enhanced source of information should, in turn, improve the ability

of the U.S. EPA (*via* tools such as MICHTOX) to evaluate the effect of atrazine use management decisions on atmospheric loadings of atrazine to Lake Michigan.

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Appendix A: Readme.Txt File

readme.txt

This readme file contains documentation for the predicted atrazine emissions produced by the Pesticide Emission Model (PEM) at Canadian ORTECH Environmental for the LMMB study. There are two files on the CD: atrazine.tar and readme.txt.

The atrazine.tar file is a unix tar file containing five (5) output files for hourly atrazine emissions. The time periods covered by the 5 files are consistent with the MM5-PX meteorological input files. The 5 file names are:

```
apr1_23.ems.gz
apr23_may16.ems.gz
may16_jun7.ems.gz
jun7_30.ems.gz
jun30_jly16.ems.gz
```

The first part of the file name indicates the time period covered by the file. The ".ems" indicates that it is an emission output file from PEM while the ".gz" indicates that the file has been compressed using the unix function "gzip" (to uncompress, use the unix function "gunzip" or use "winzip" on a Windows platform).

A sample FORTRAN read statement is as follows:

```
      read(3,22) itb, itc, ith, latc, lonc, emission
22    format(3(i2,1x),2(f7.2,1x),e13.7,1x)
```

where: itb - month
 itc - day
 ith - hour
 latc - cell centroid latitude north (decimal degrees)
 lonc - cell centroid longitude west (decimal degrees)
 emission - hourly atrazine emission (kg/grid)

The sequence in which the hourly atrazine emissions are given in the files is similar to the method used for the MM5-PX meteorological files in that all the hourly atrazine emissions are given for the entire domain (starting at the south-west corner of the domain) before advancing to the next hour.

Table 2.1: Soil parameters.

Soil Class	Soil Texture Description	Field Capacity ⁺ , θ_{fc} (Vol. Fract.)	Saturation Capacity [*] , θ_s (Vol. Fract.)	Wilt Point ⁺ , θ_w (Vol. Fract.)	Saturation Hydraulic Conductivity [*] , k_s (10^{-6} m/s)	Soil Constant [*] , b	Saturation Matrix Potential [*] , ψ_s (m)
1	Sand	0.135	0.395	0.068	176	4.05	0.121
2	Loamy Sand	0.150	0.410	0.075	156	4.38	0.090
3	Sandy Loam	0.195	0.435	0.114	34.7	4.90	0.218
4	Silt Loam	0.255	0.485	0.179	7.20	5.30	0.786
5	Loam	0.240	0.451	0.155	6.95	5.39	0.478
6	Sandy Clay Loam	0.255	0.420	0.175	6.30	7.12	0.299
7	Silty Clay Loam	0.322	0.477	0.218	1.70	7.75	0.356
8	Clay Loam	0.325	0.476	0.250	2.45	8.52	0.630
9	Sandy Clay	0.310	0.426	0.219	2.17	10.4	0.153
10	Silty Clay	0.370	0.492	0.283	1.03	10.4	0.490
11	Clay	0.367	0.482	0.286	1.28	11.4	0.405
12	Rock	0	0	0	--	--	--

* taken from Clapp and Hornberger (1978)

⁺ taken from Lee and Pielke (1992)

Table 3.1: Summary of atrazine volatilization data in the literature.

Author	Field or Lab	Soil Conditions	Meteorological Conditions	Sampling Period	Percent Volatilized	Comments
Glotfelty <i>et al.</i> , 1989	• field (May-June, 1981, Maryland)	• silt loam • $f_{oc}=1.5\%$ • conventional till	• wind speed: 0.5-5.5 m/s • air temp.: 24-32 °C • # of precip. events: 4 • total precip.: 40 mm	21 days	2.4 %	• suspects that wind erosion contributes to the total percent volatilized
Clendening <i>et al.</i> , 1990	• field (Oct.- Nov., 1986, California)	• sandy loam • “low organic carbon content”	• # of irrigations: 3 • avg. water applied: 60 mm • no meteorology data published	3 days 17 days	0.16% 0.43% ⁺	• atrazine initially dissolved with acetone to increase solubility
Whang <i>et al.</i> , 1993	• field (April, 1990, Maryland)	• loamy sand • $f_{oc}=NA\%$ • conventional and no till	• avg. wind speed: NA m/s • air temp.: -4-+33°C • # of precip. events: 5 • total precip.: 87 mm	4 days 26 days	0.7% (till) 0.9% (no till) 1.9%* (till) 2.5%* (no till)	• side-by-side field experiment for conventional and no till practices
Wienhold and Gish, 1994	• field, (June, 1992, Maryland)	• sandy loam • $f_{oc}=1.1\%$ • conventional and no till	• avg. wind speed: 0.1 m/s • air temp.: 7-32 °C • # of precip. events: 13 • total precip.: 106 mm	35 days	9% (till) 4% (no till)	
Gish <i>et al.</i> , 1995	• lab, no date	• sandy loam • $f_{oc}=1.1\%$	• const. Wind speed: 0.1 m/s • air temp.: 25 & 35 °C • # of irrigation events: 10 • total irrigation: 100 mm	30 days	4% (25 °C) 9% (35 °C)	• differences in literature values are due to drying, nightly cooling, soil types, and precipitation
Rice <i>et al.</i> , 1998	• field (May-June, 1995, Maryland)	• silt loam • $f_{oc}\approx 0.97\%$	• measured wind speed, temperature, humidity, rain, radiation intensity and soil moisture and temperatures	4 days 21 days	2.1% 3.6%	

⁺ value derived by integrating the volatilization flux time series (given in Figure 1 of Clendening *et al.*, 1990) for 17 days.

* Wang *et al* (1993) estimated value based on 26 days of measurements.

Table 3.2: Summary of predicted atrazine volatilization versus dispersion coefficient.

Dispersion Coefficient, λ	Day 21	Day 26	Day 30	Day 35
$\lambda = 0.003$ m	8.1 %	9.2 %	10.4 %	11.5 %
$\lambda = 0.005$ m	6.5 %	7.3 %	8.3 %	9.1%
$\lambda = 0.010$ m	4.7 %	5.3 %	6.0 %	6.6 %
$\lambda = 0.020$ m	3.4 %	3.9 %	4.4 %	4.8 %

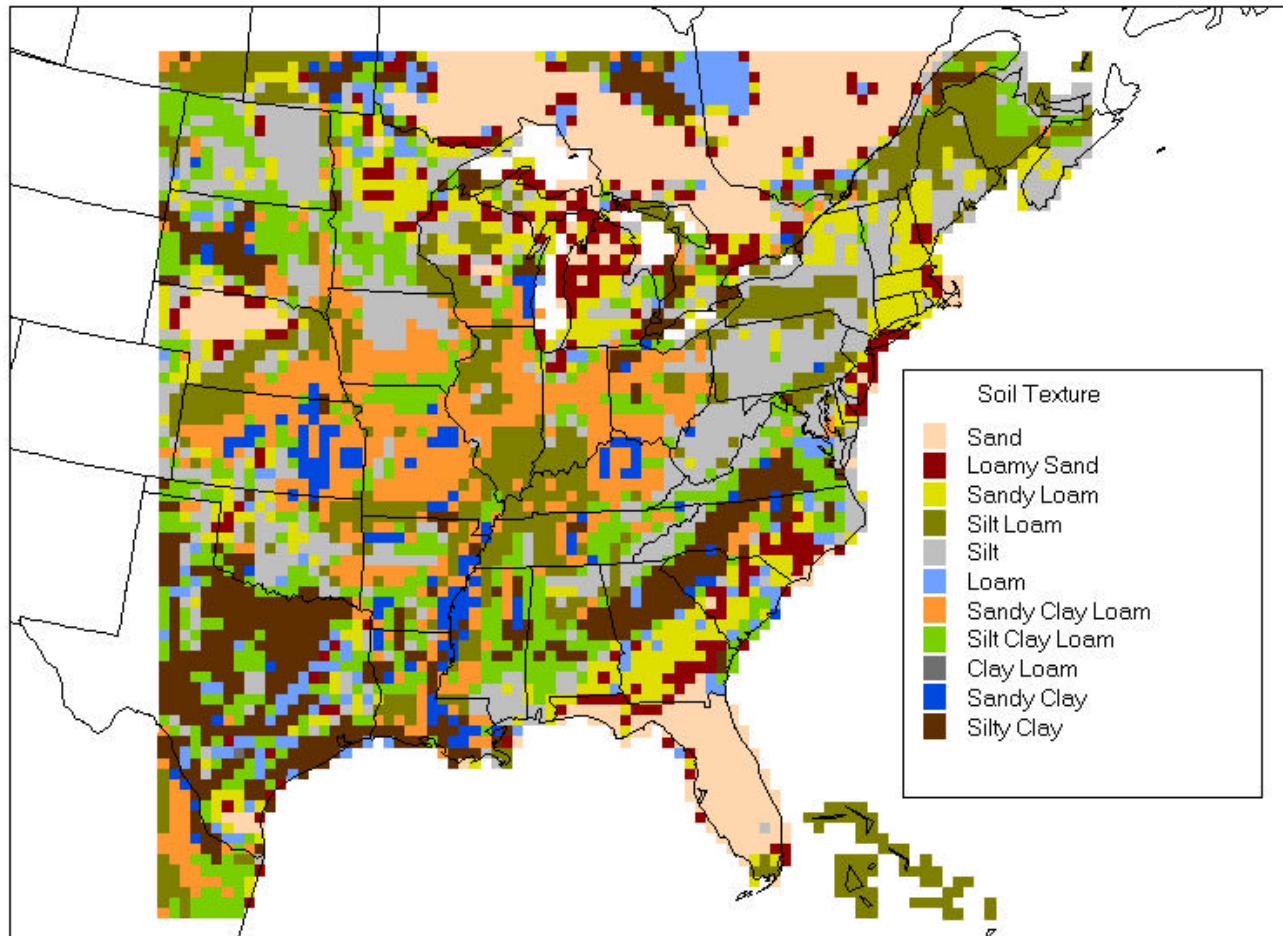


Figure 2.1: Gridded soil texture

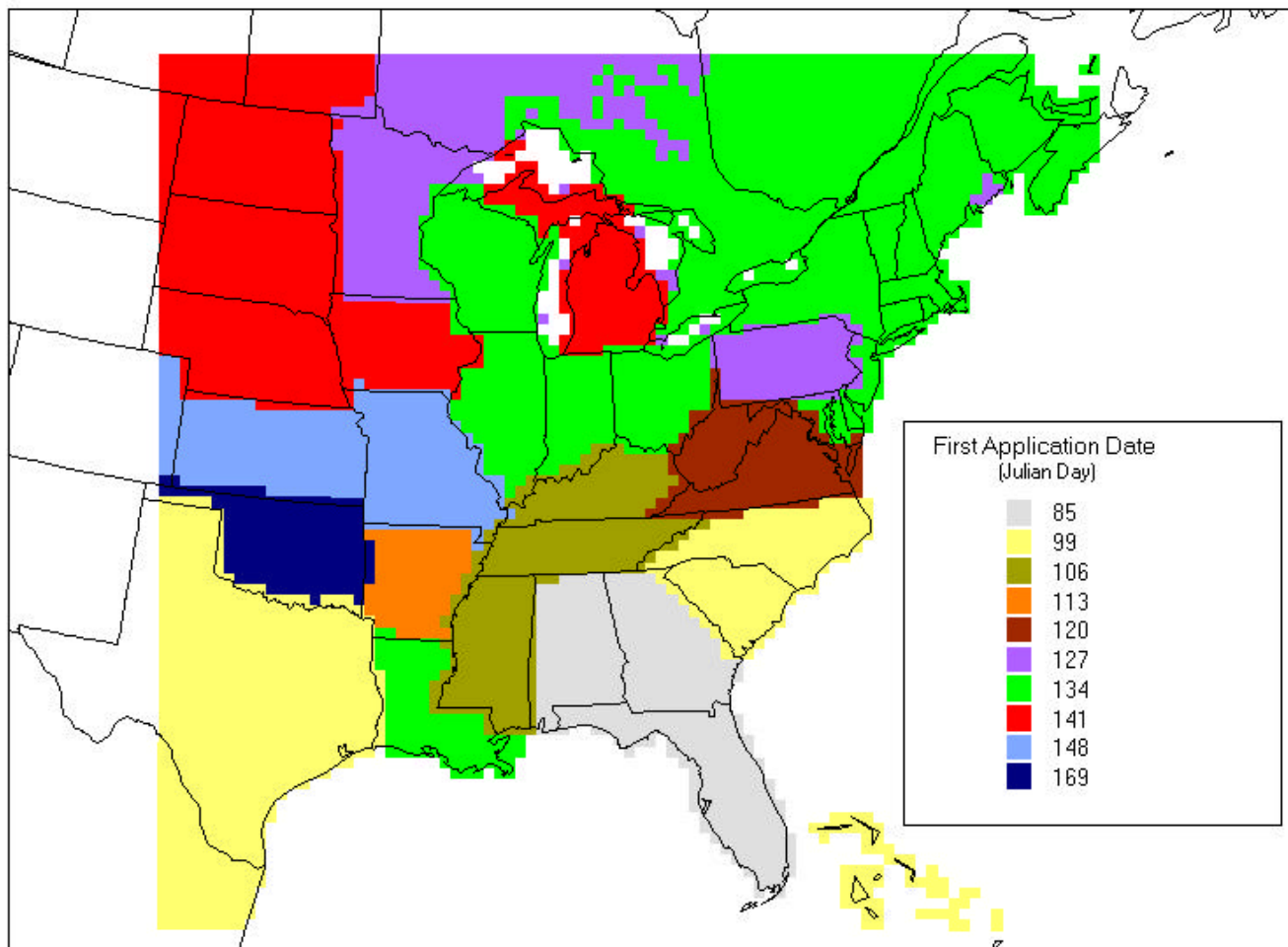


Figure 2.2: First atrazine application date.

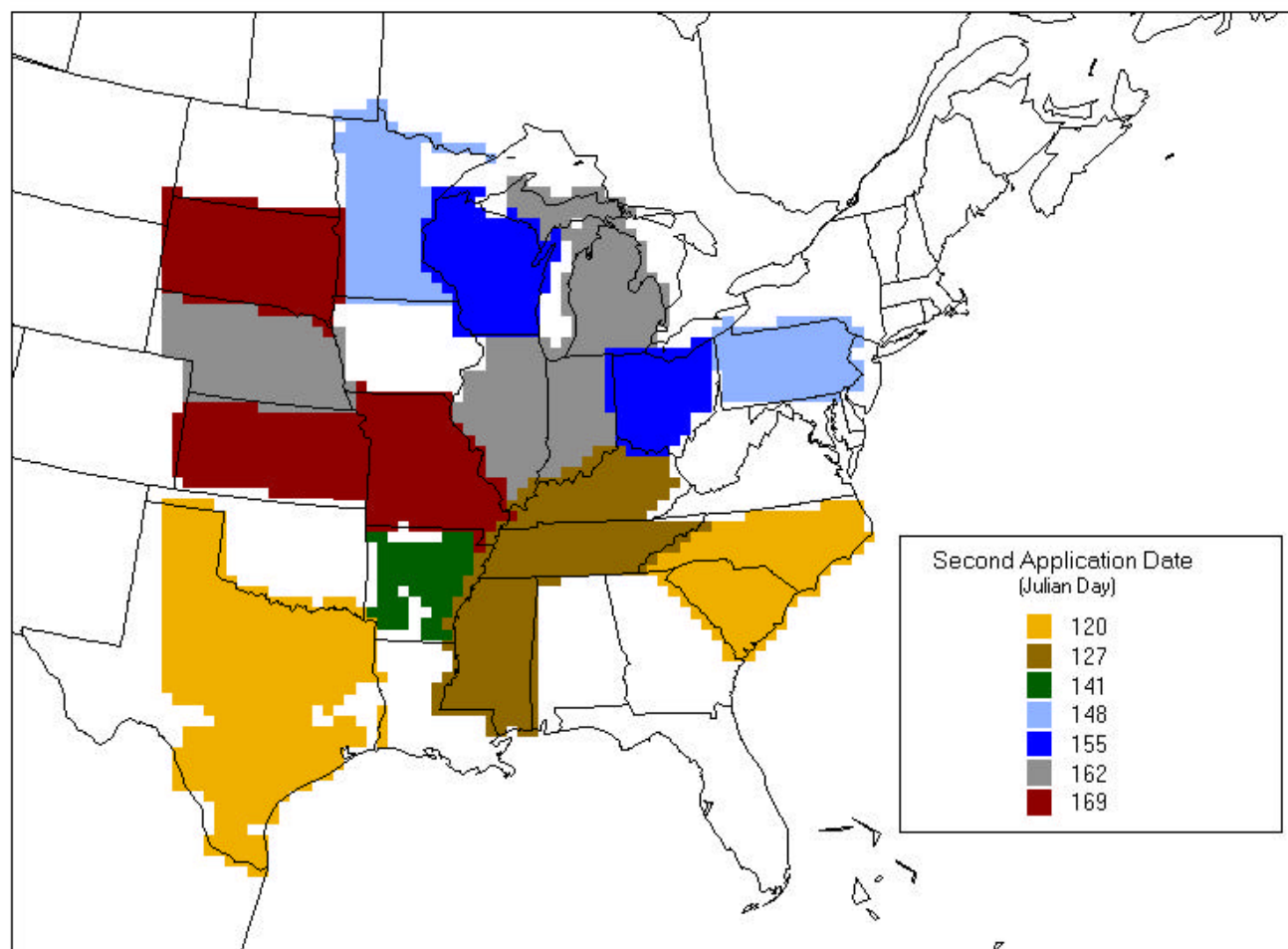


Figure 2.3: Second atrazine application date.

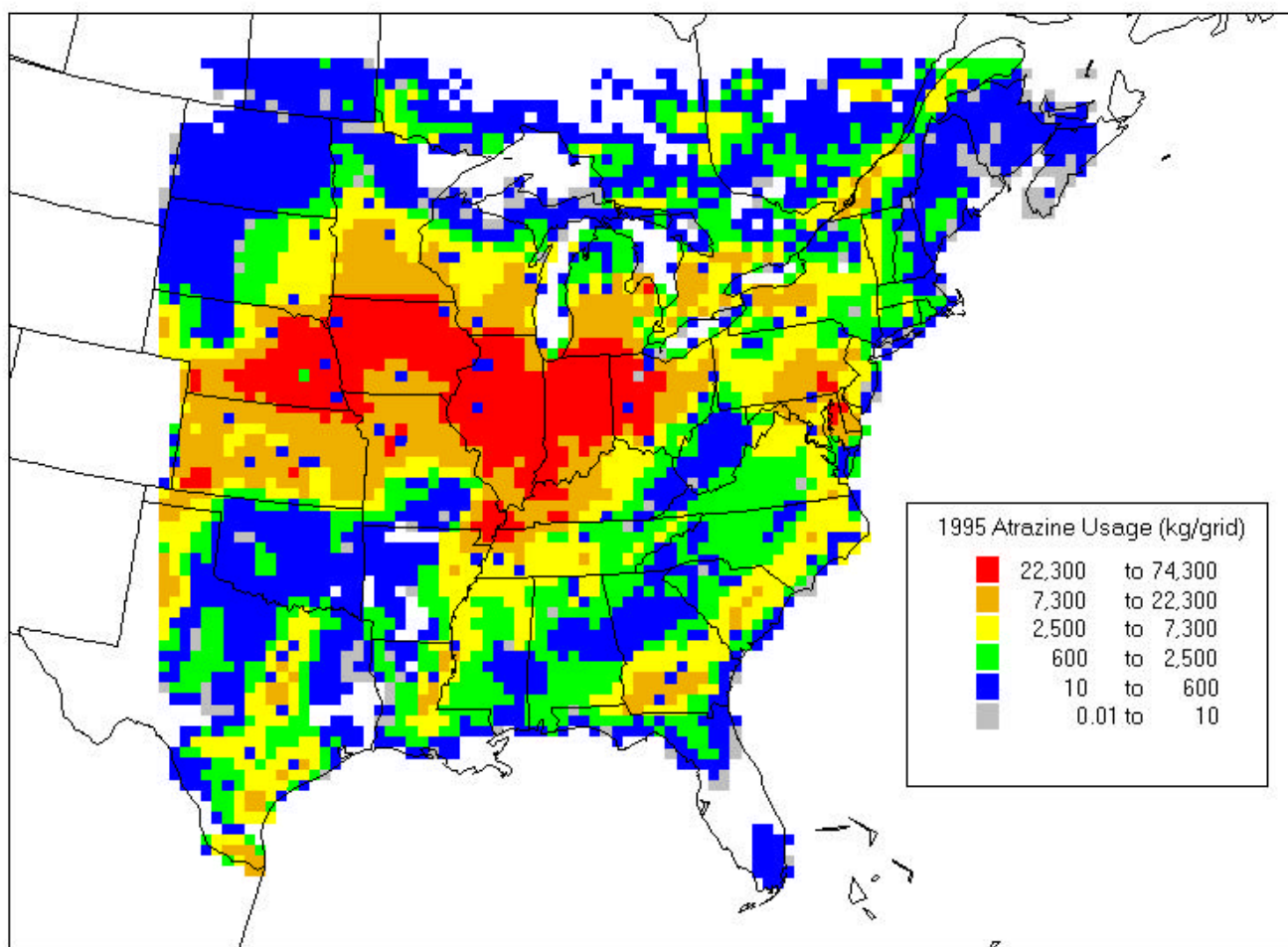


Figure 2.4: 1995 gridded atrazine usage.

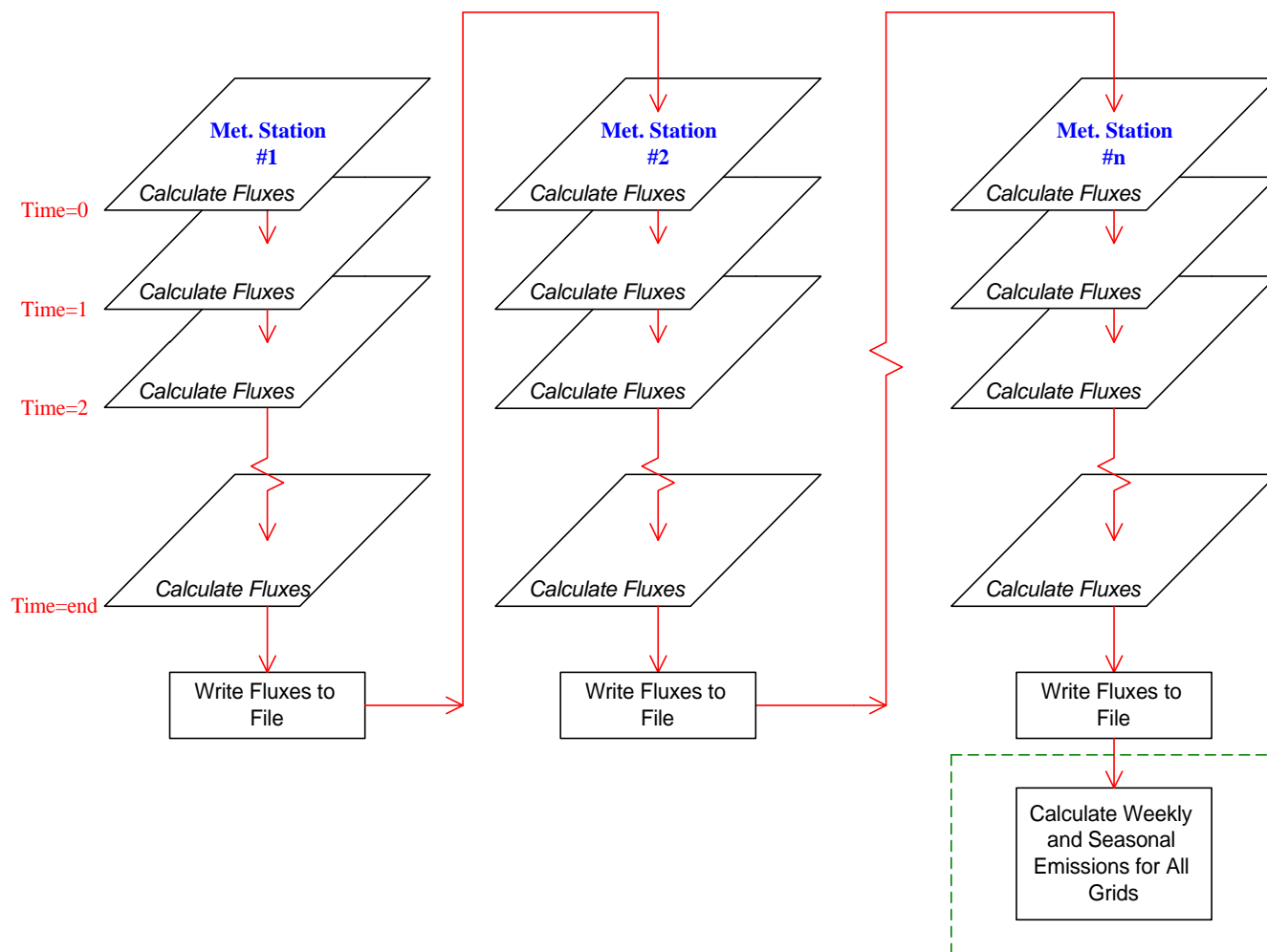


Figure 3.1: Logic schematic of the original pesticide emission model.

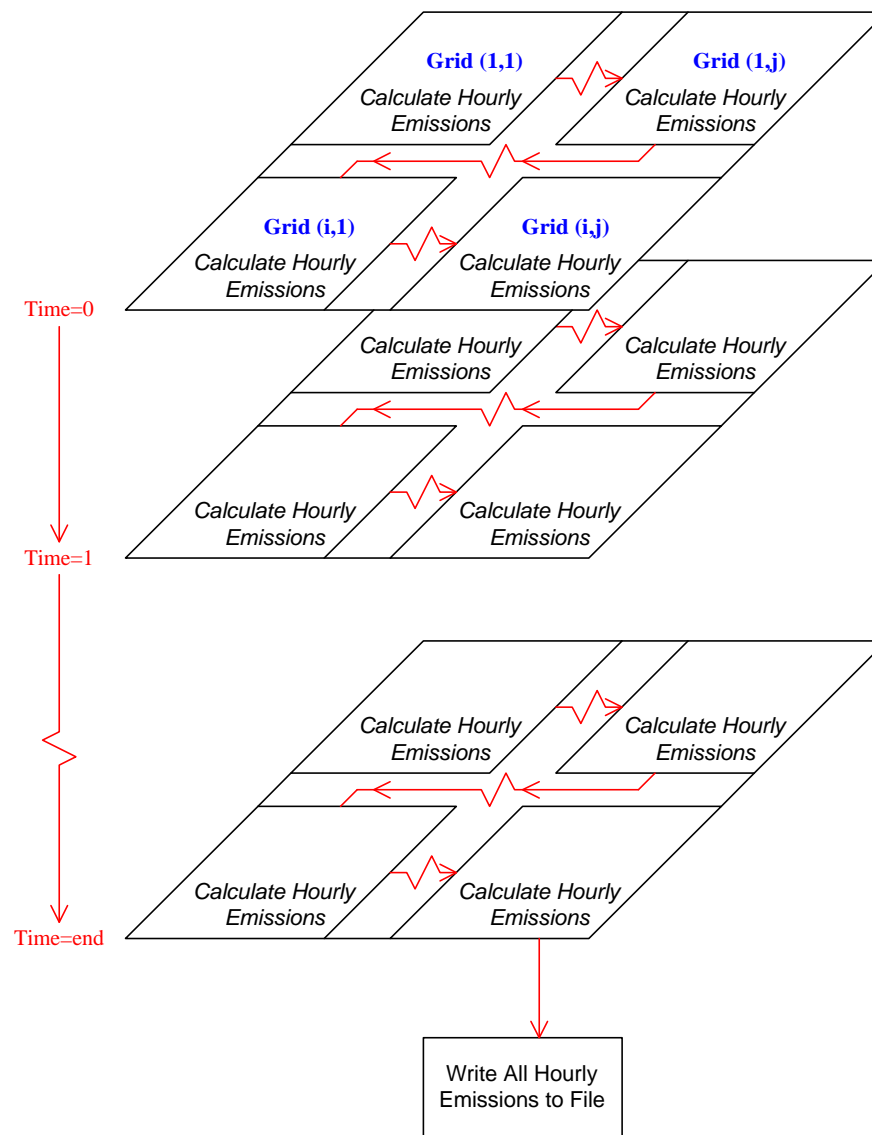


Figure 3.2: Logic schematic of the episodic pesticide emissions model

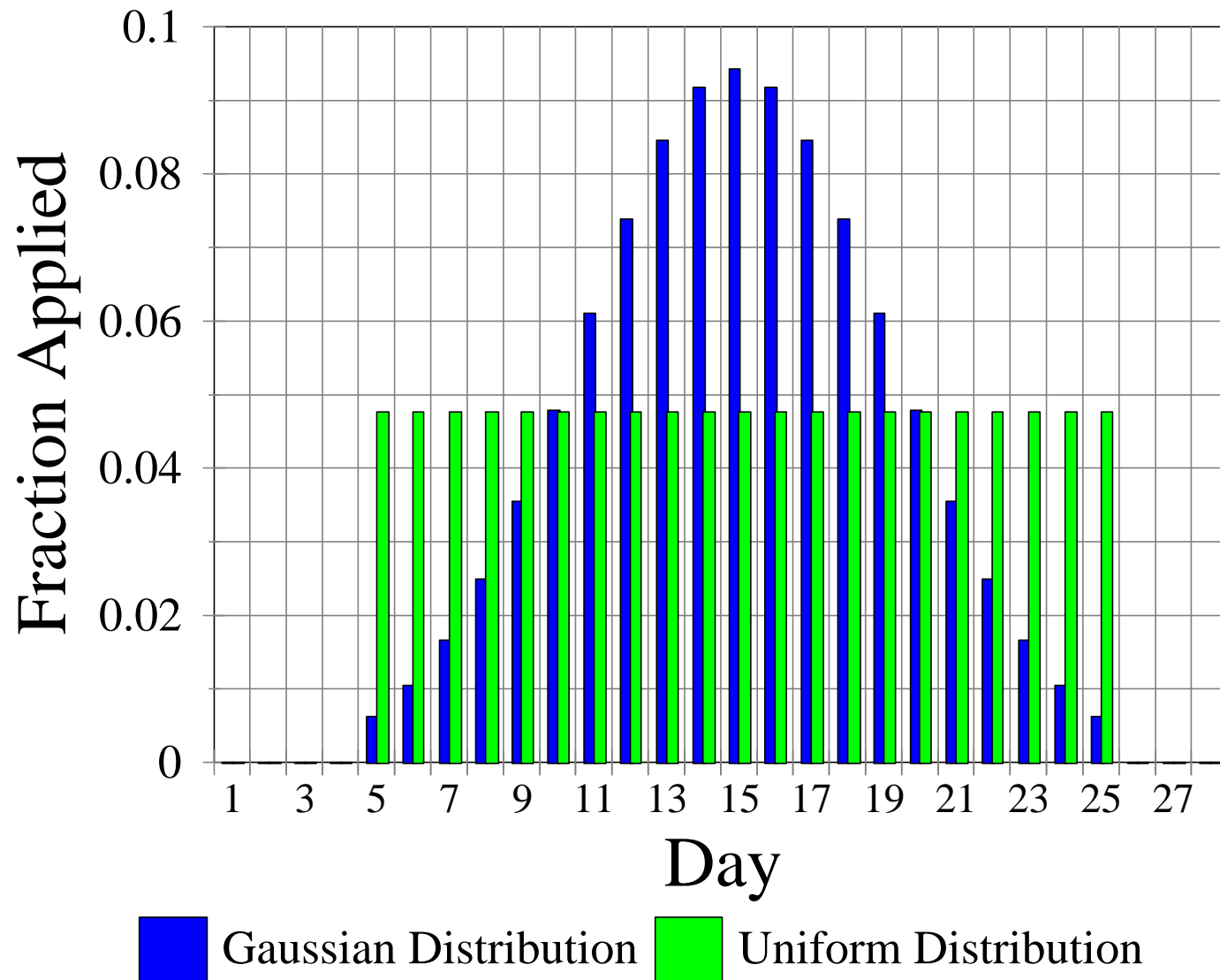


Figure 3.3: Distributed atrazine application over a three week period centered on day 15 assuming an application rate of unity.

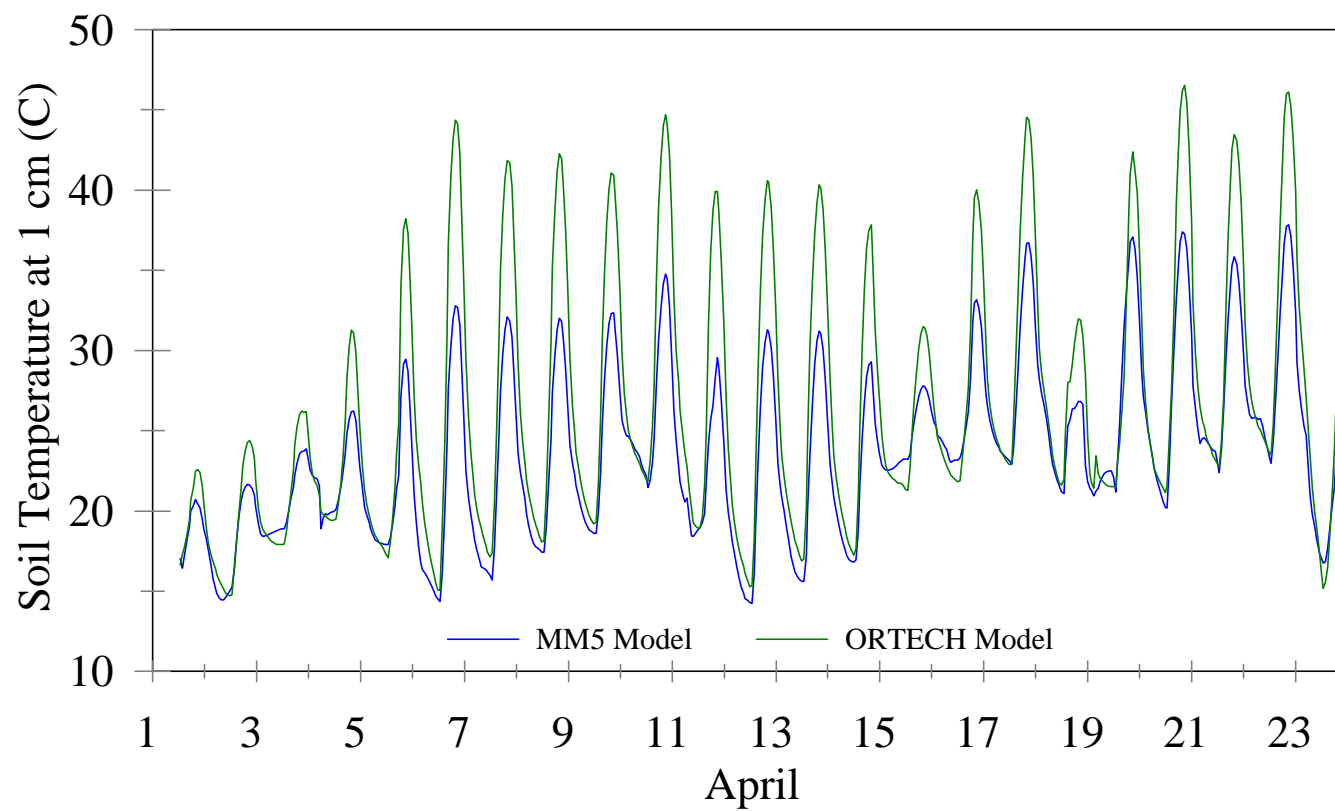


Figure 3.4: Comparison of the predicted soil temperatures at 1 cm between PEM and the MM5-PX model when PEM is using a “local: scale in calculating the transport of heat and moisture.

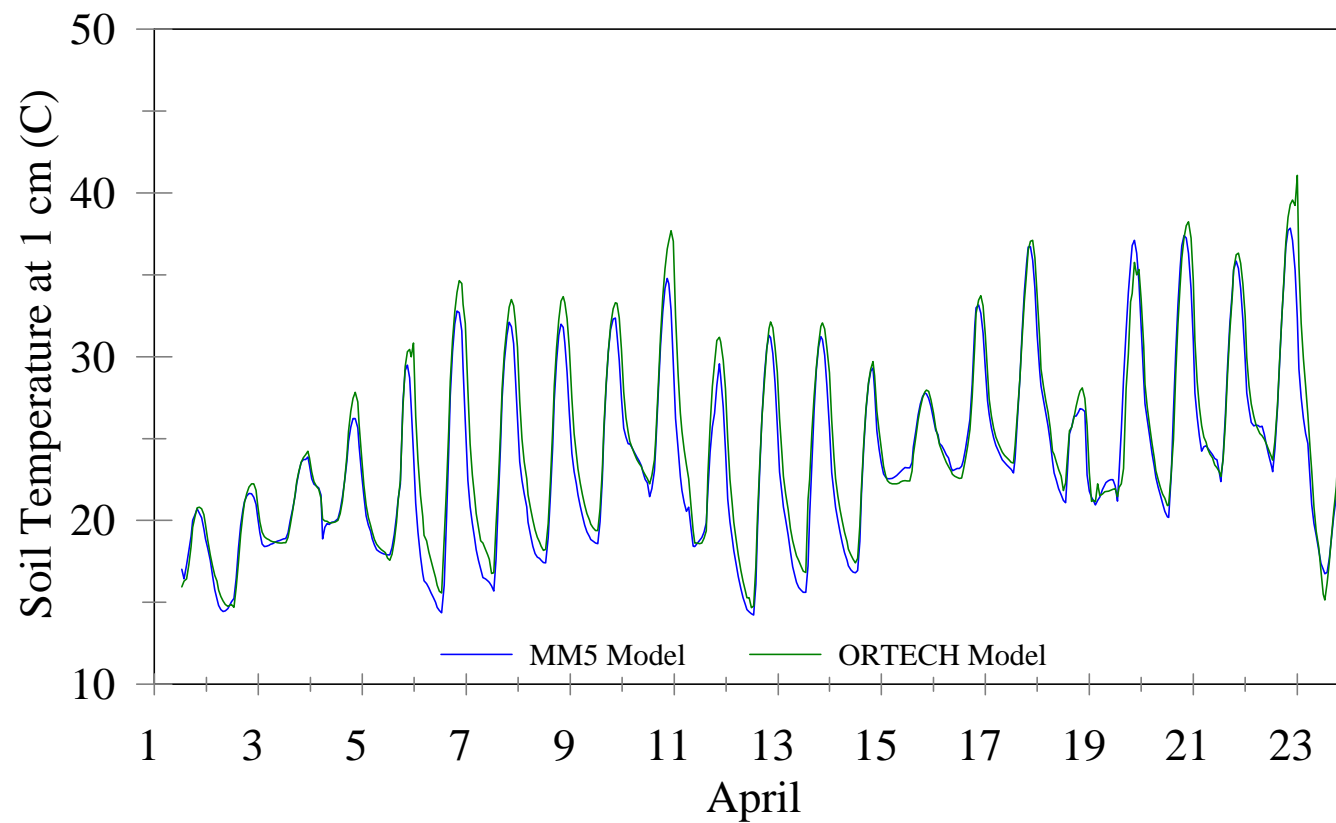


Figure 3.5: Comparison of the predicted soil temperatures at 1 cm between PEM and the MM5-PX model when PEM is using the MM5-PX “regional” scale in calculating the transport of heat and moisture.

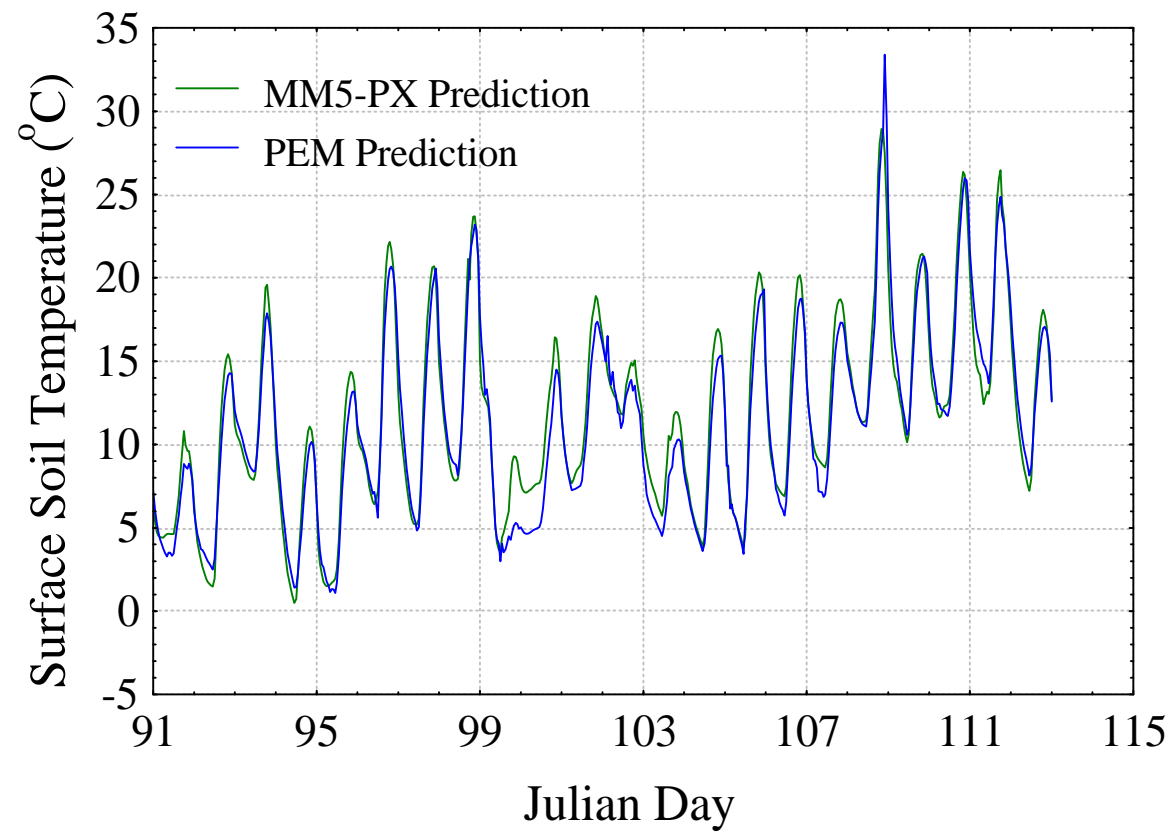


Figure 4.1: Comparison of surface soil temperature predictions for a grid cell in Maryland (lat/long: 39.00/-76.87).

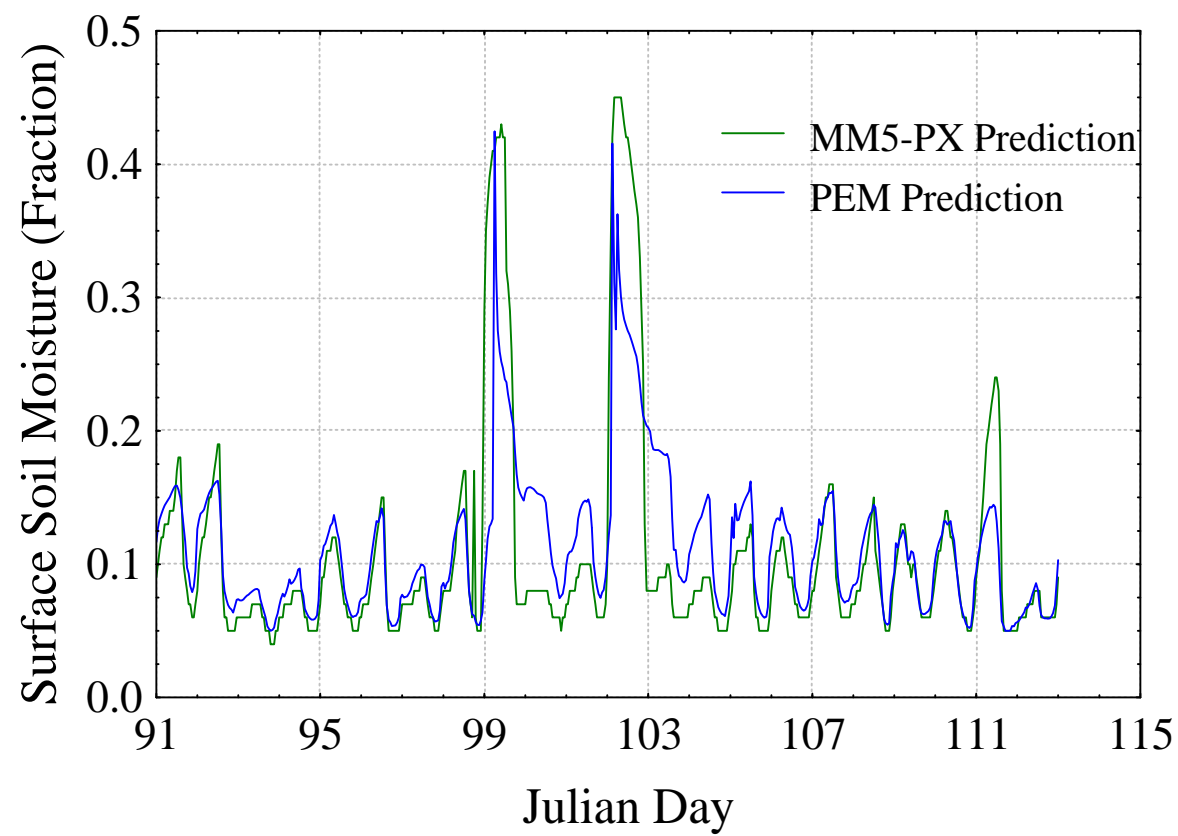


Figure 4.2: Comparison of surface soil moisture predictions for a grid cell in Maryland (lat/long: 39.00/-76.87).

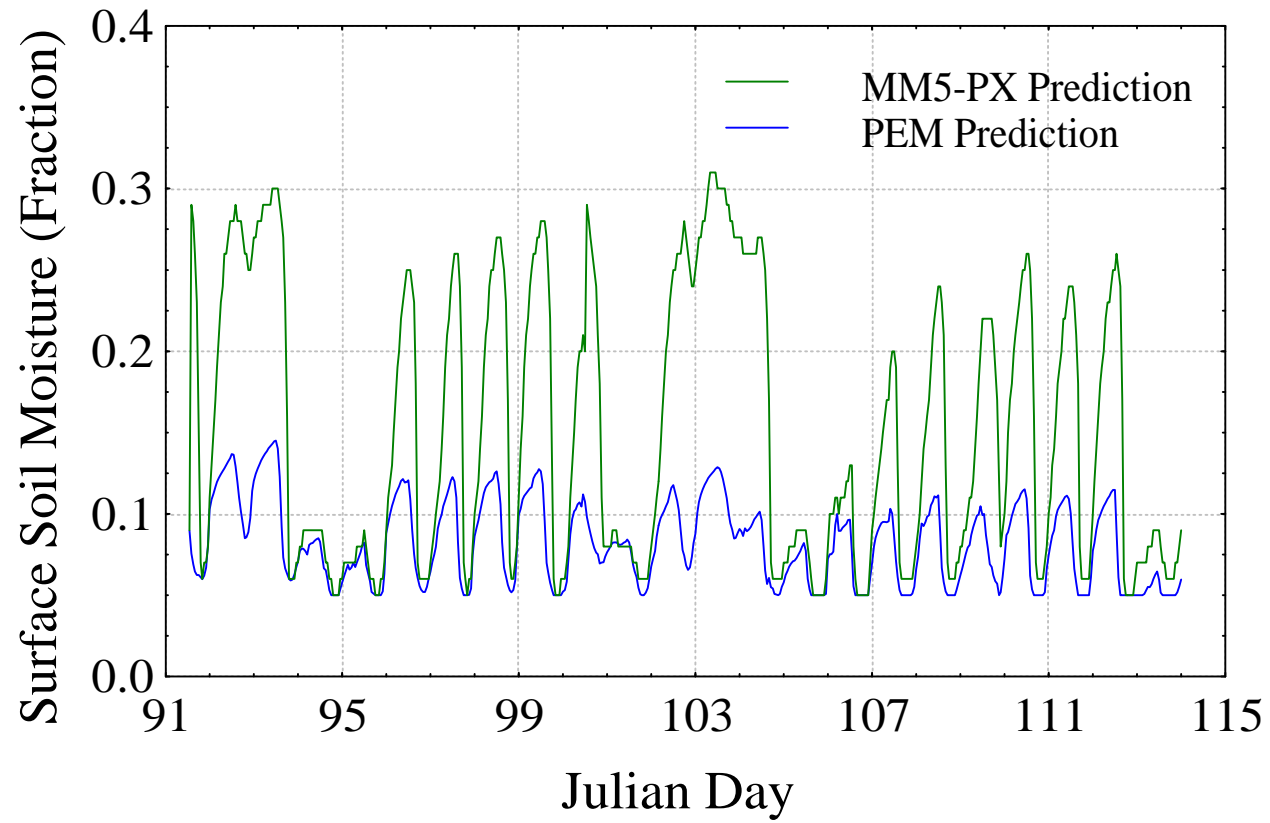


Figure 4.3: Comparison of surface soil moisture predictions for a grid cell in Delaware (lat/long: 38.50/-75.68).

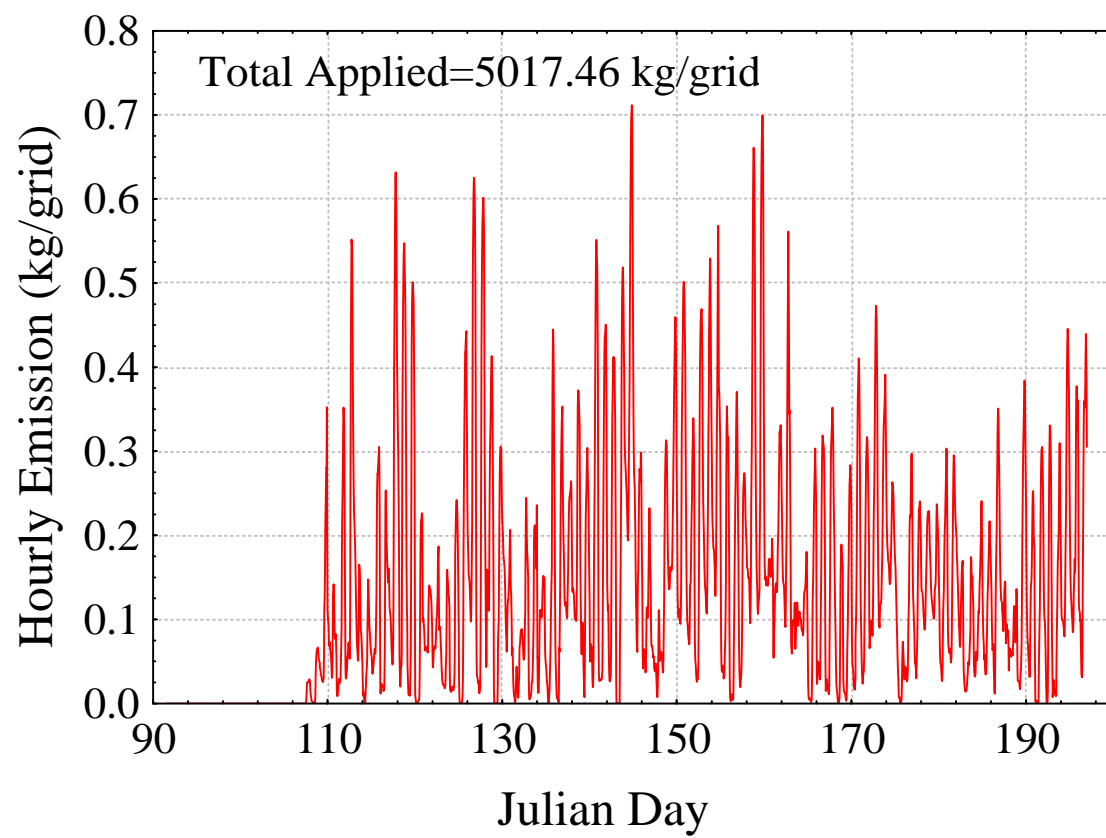


Figure 4.4: Hourly atrazine emissions for a grid cell in Maryland (lat/long: 39.00/-76.87).

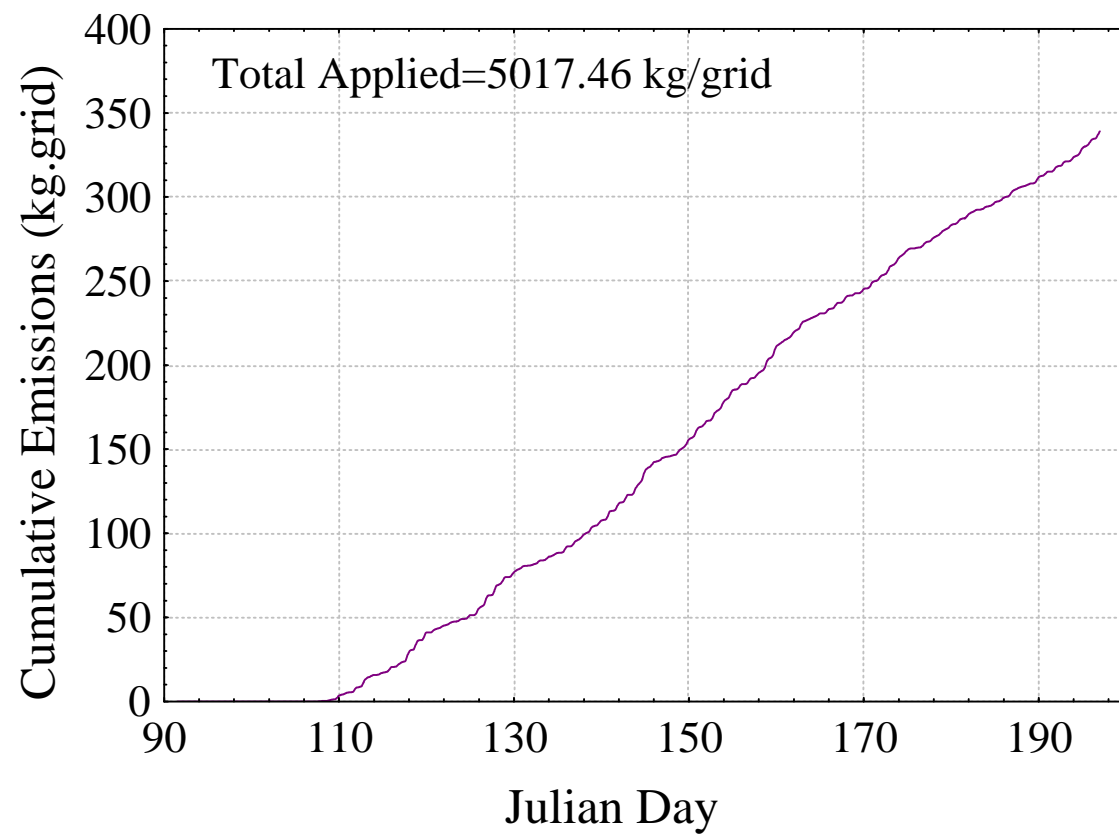


Figure 4.5: Cumulative atrazine emissions for a grid cell in Maryland (lat/long: 39.00/-76.87).

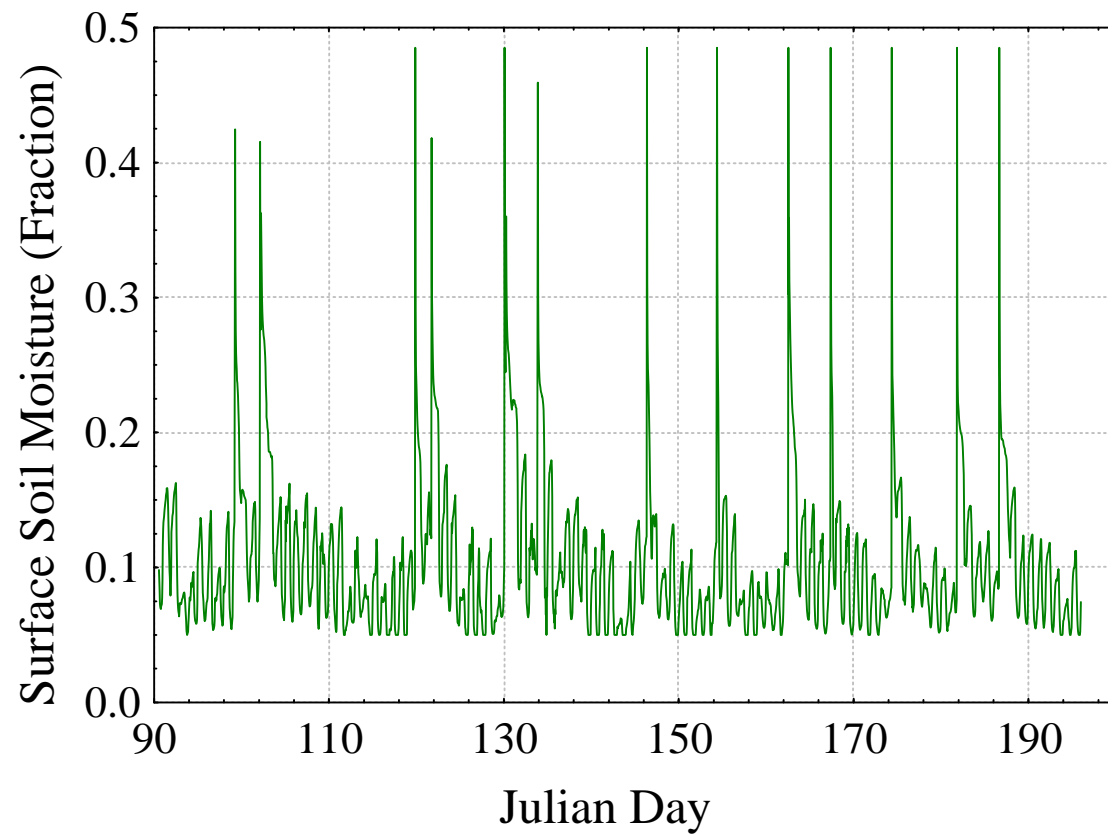


Figure 4.6: Surface soil moisture for a grid cell in Maryland (lat/long: 39.00/-76.87).

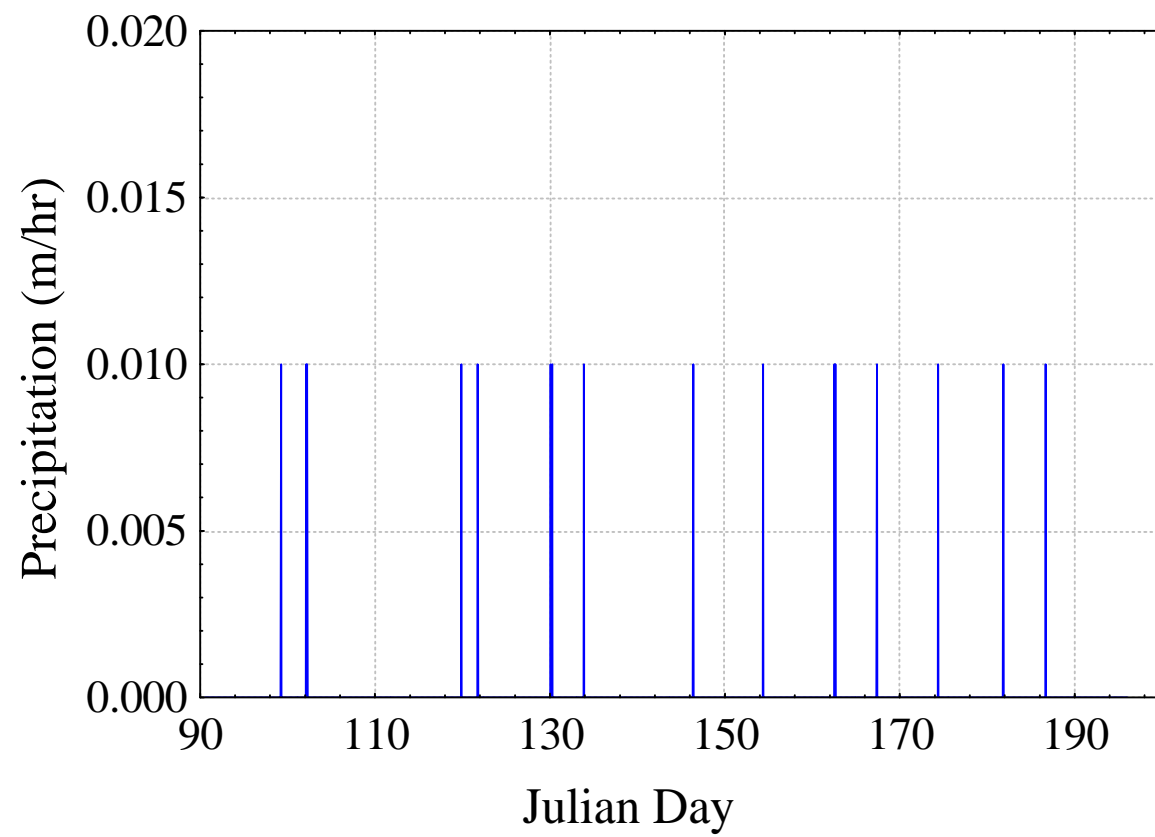


Figure 4.7: Precipitation for a grid cell in Maryland (lat/long: 39.00/-76.87).

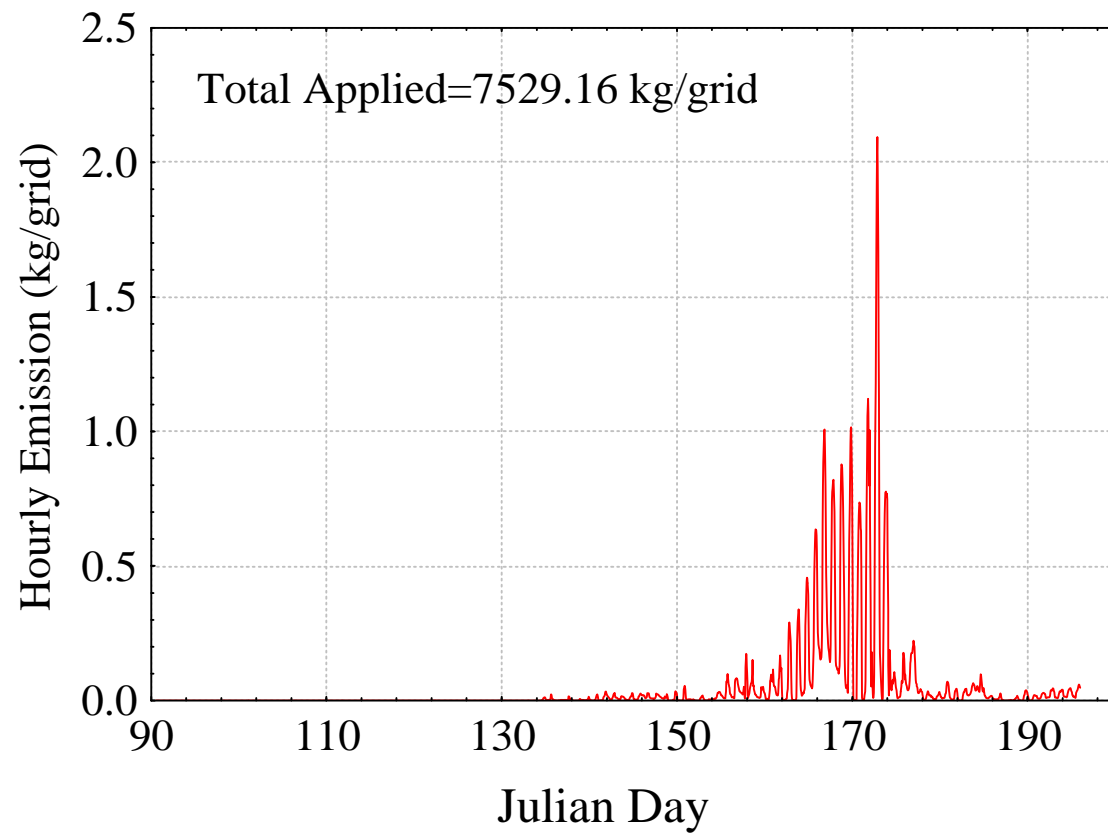


Figure 4.8: Hourly atrazine emissions for a grid cell in Northern Missouri (lat/long: 40.46/-92.85).

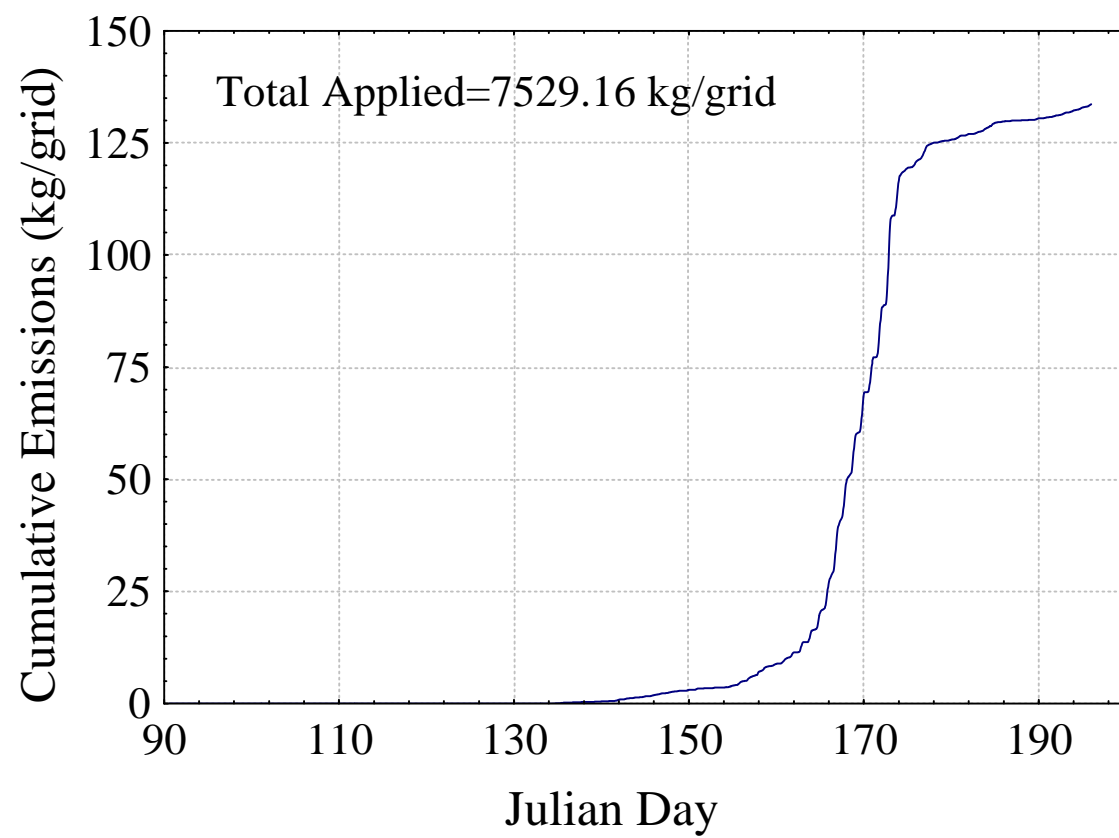


Figure 4.9: Cumulative atrazine emissions for a grid cell in Northern Missouri (lat/long: 40.46/-92.85).

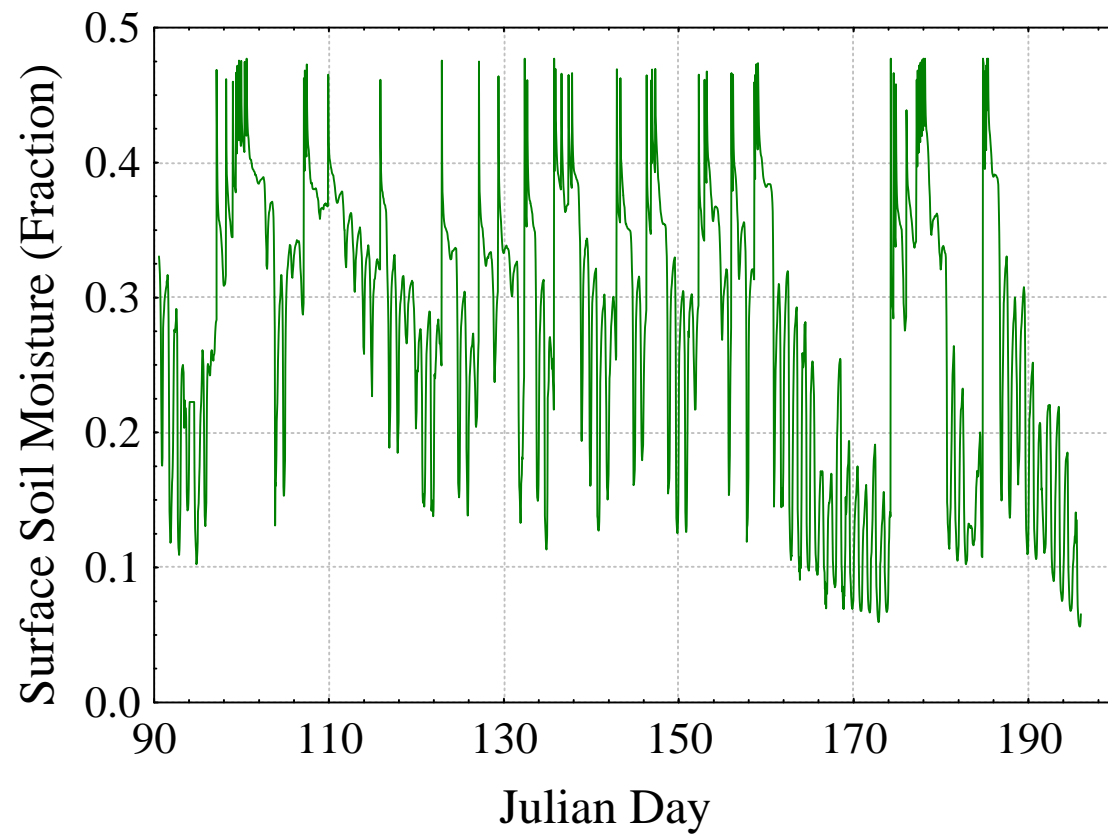


Figure 4.10: Surface Soil Moisture for a grid cell in Northern Missouri (lat/long: 40.46/-92.85).

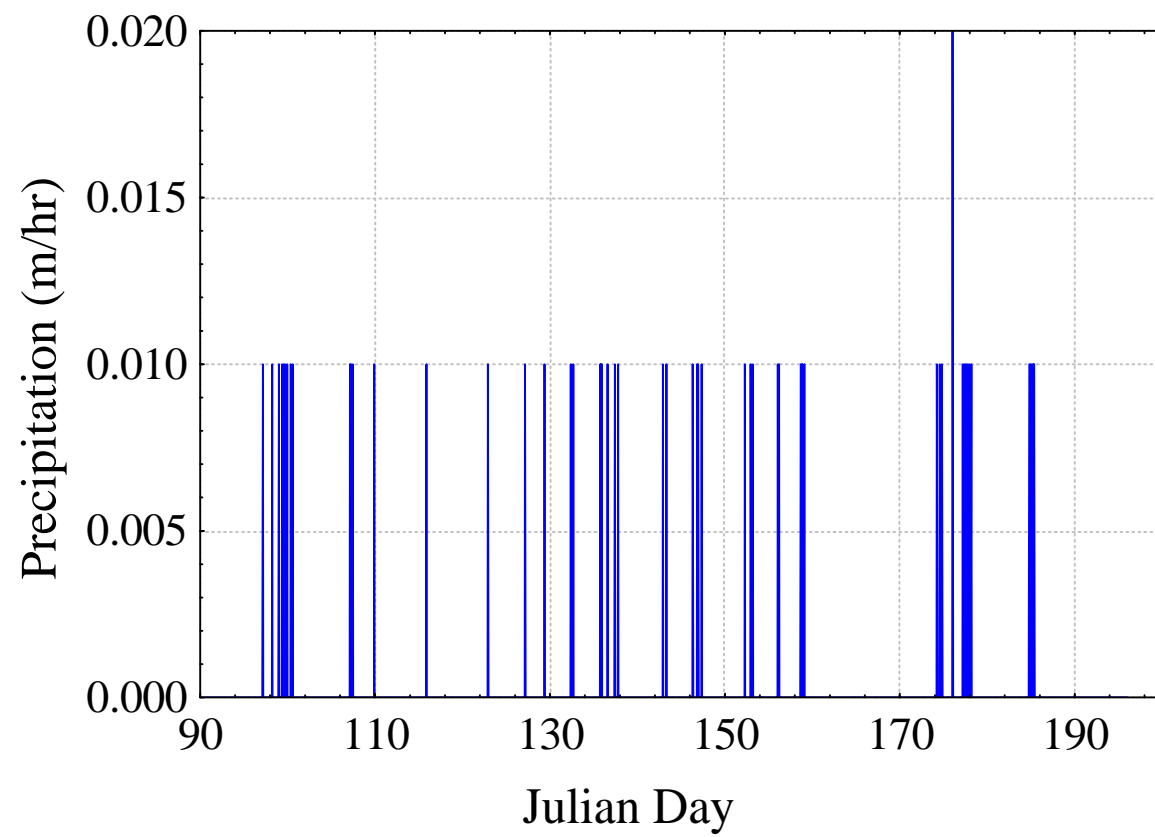


Figure 4.11: Precipitation for a grid cell in Northern Missouri (lat/long: 40.46/-92.85).

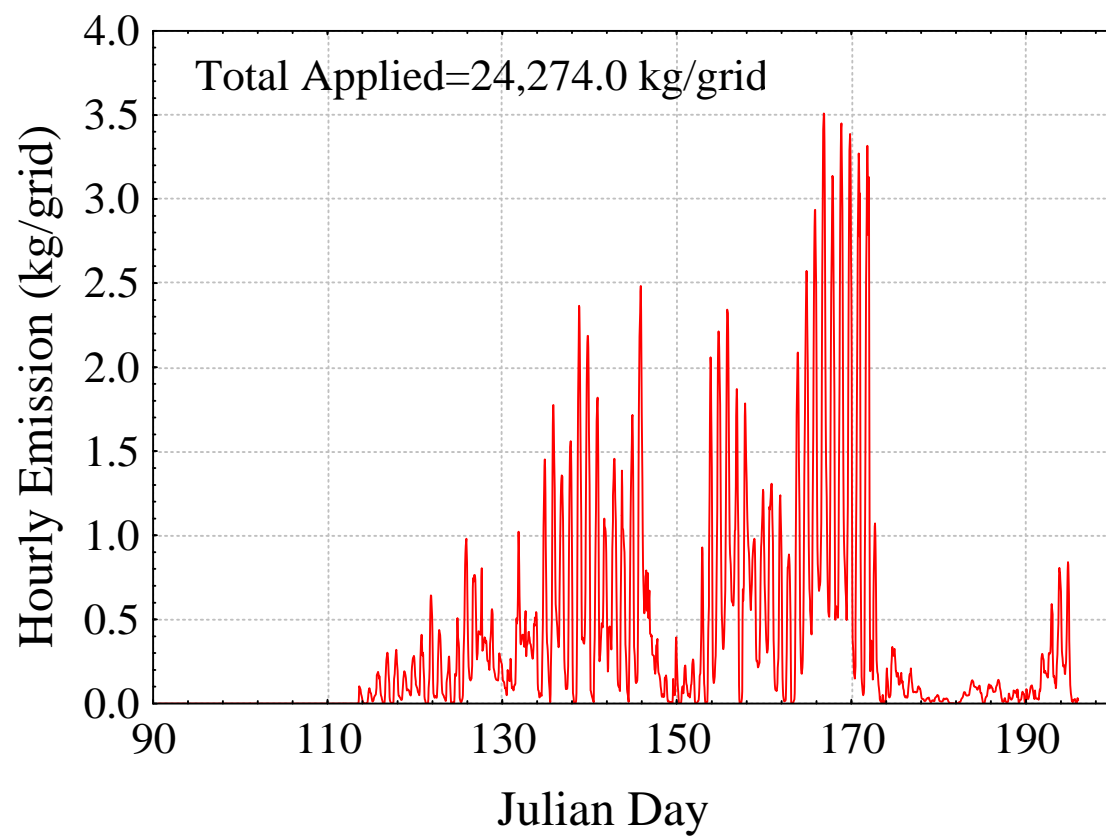


Figure 4.12: Hourly atrazine emissions for a grid cell in Northern Iowa (lat/long: 43.41/-94.84).

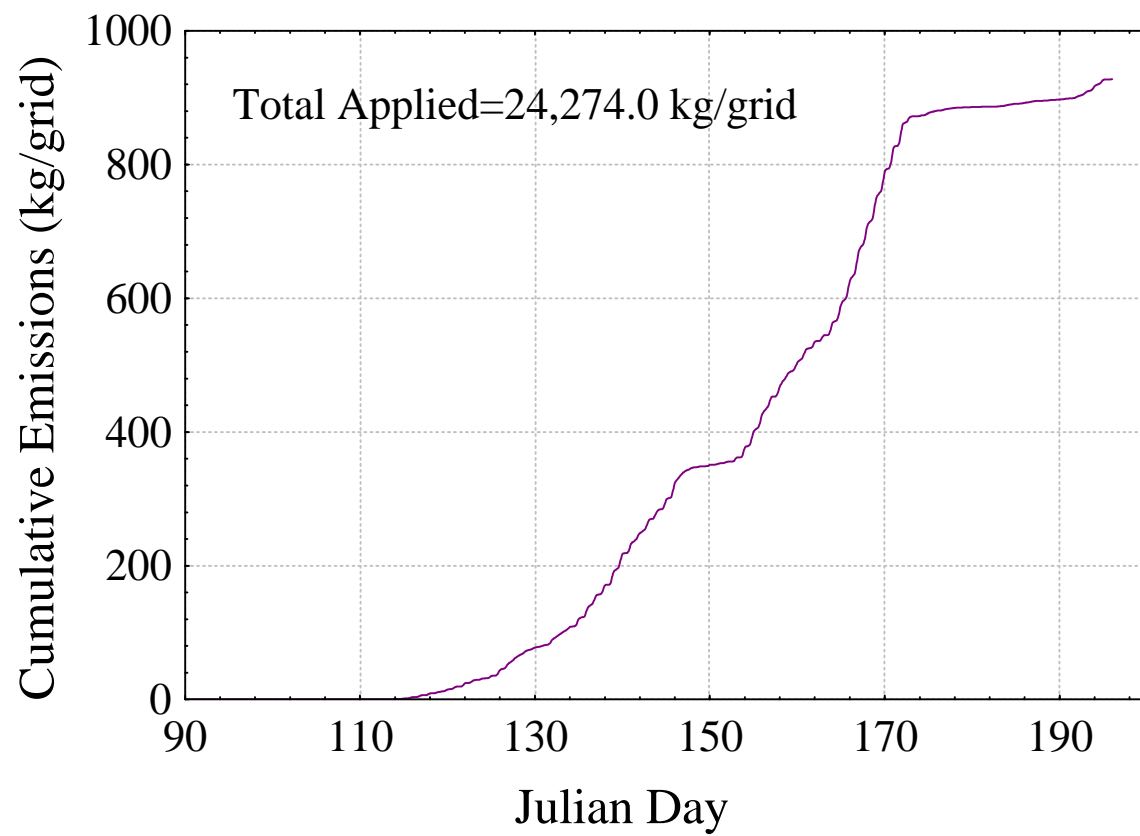


Figure 4.13: Cumulative atrazine emissions for a grid cell in Northern Iowa (lat/long:43.41/-94.84).

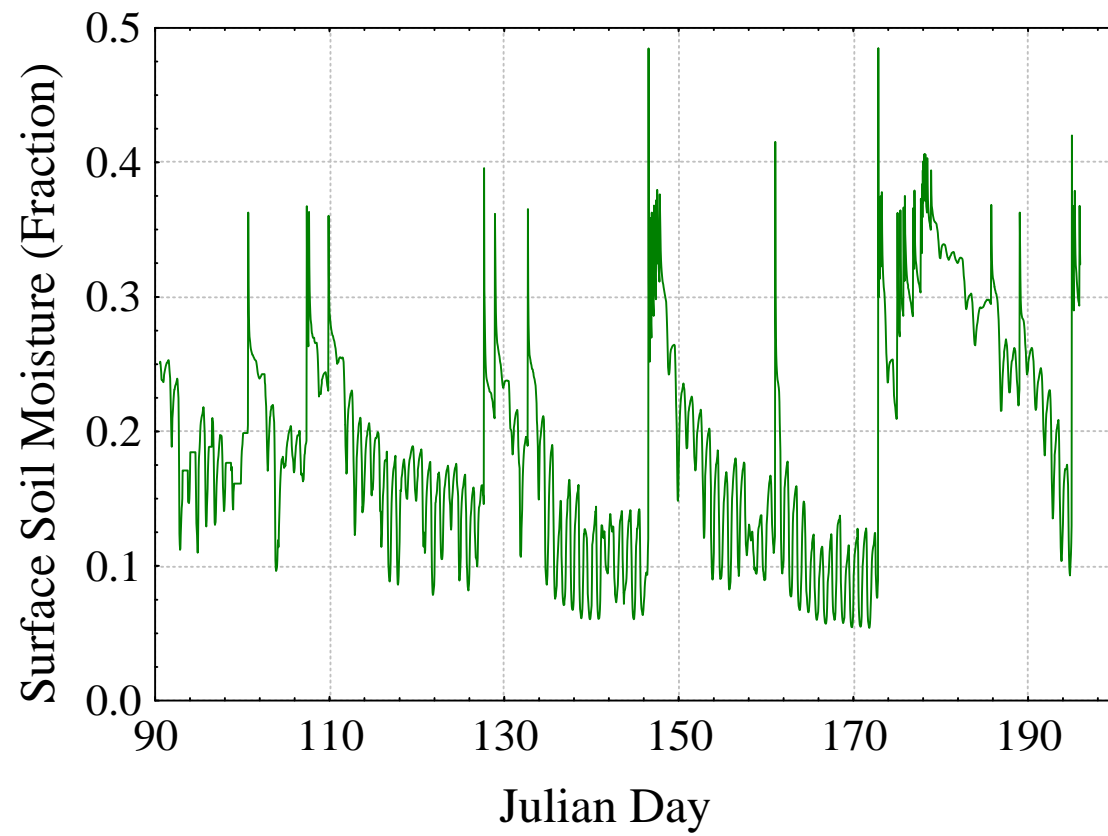


Figure 4.14: Surface soil moisture for a grid cell in Northern Iowa (lat/long: 43.41/-94.84).

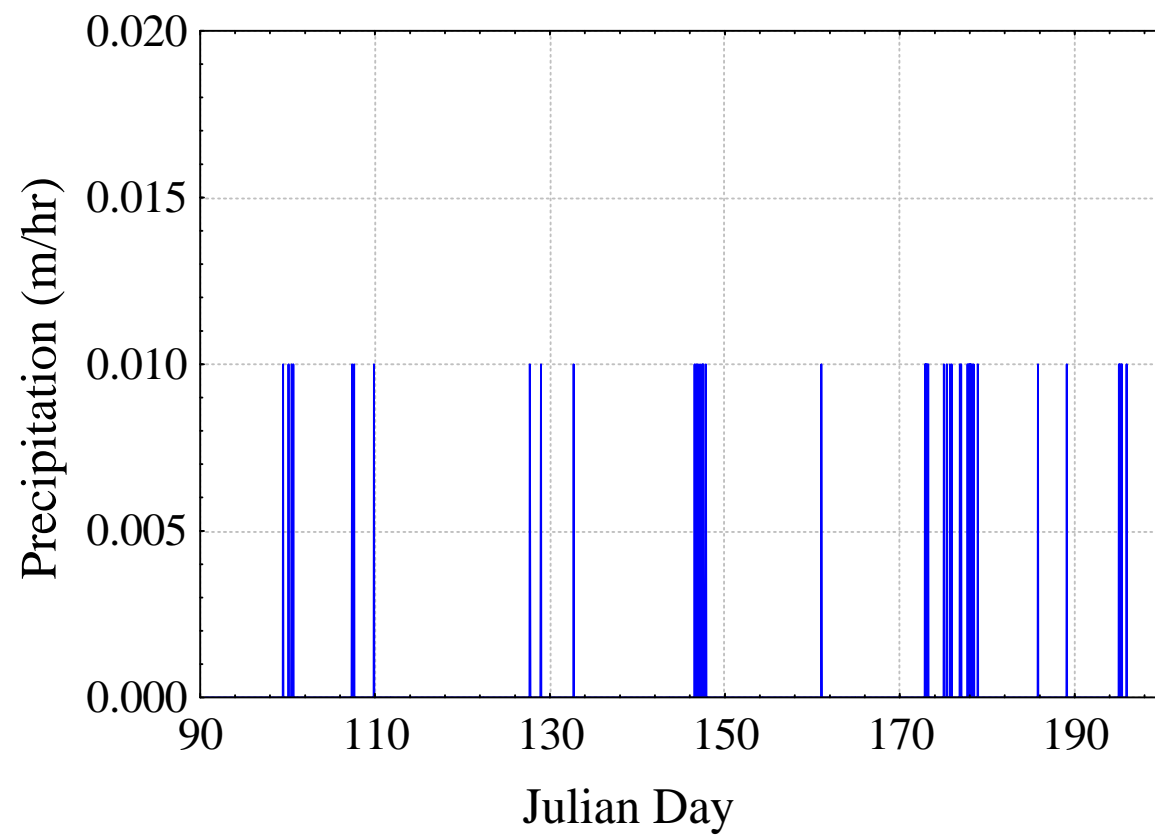


Figure 4.15: Precipitation for a grid cell in Northern Iowa (lat/long: 43.41/-94.84).

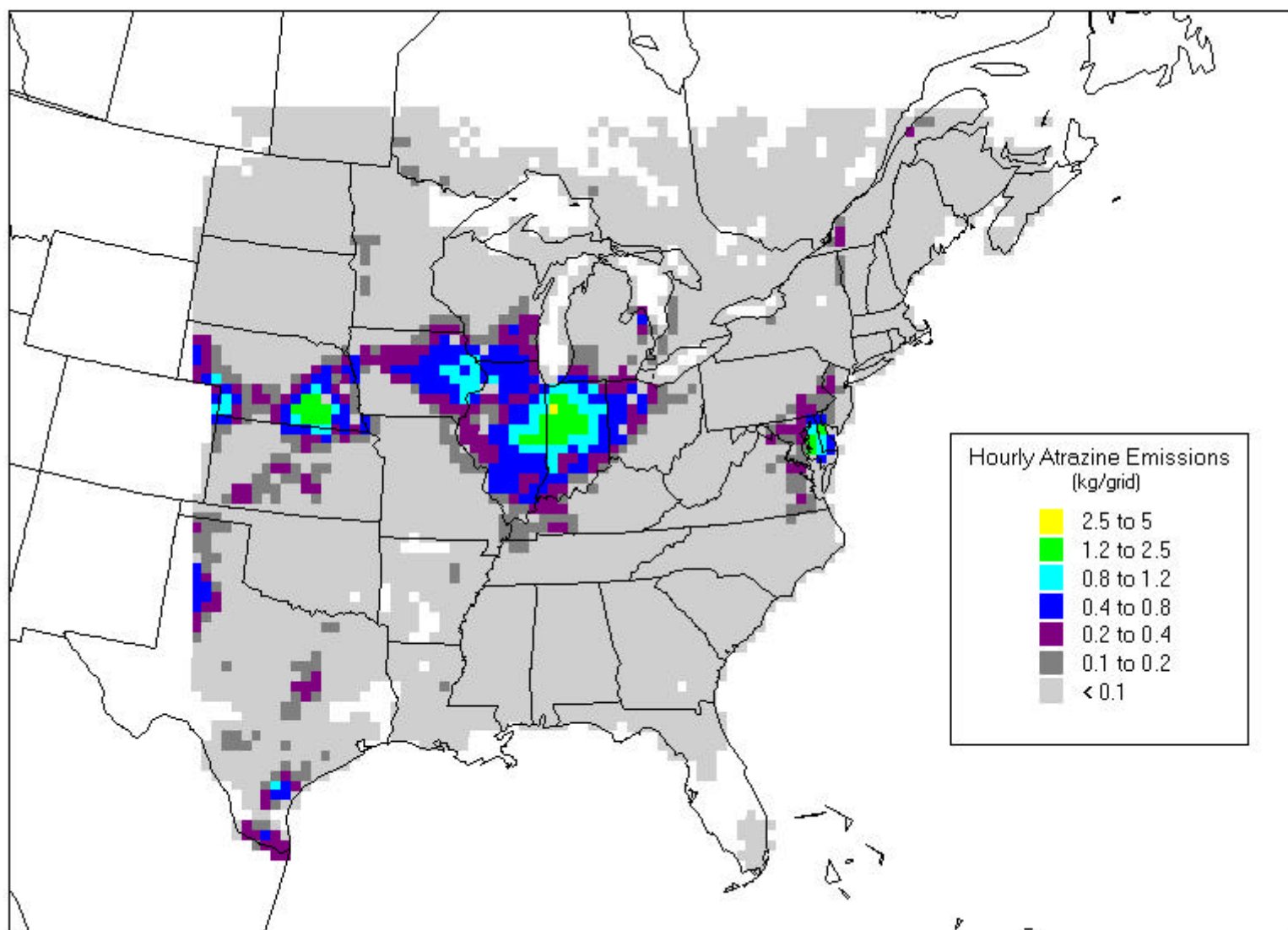


Figure 4.16: Hourly atrazine emissions for Julian day 158 at 07:00 UT (02:00EST).

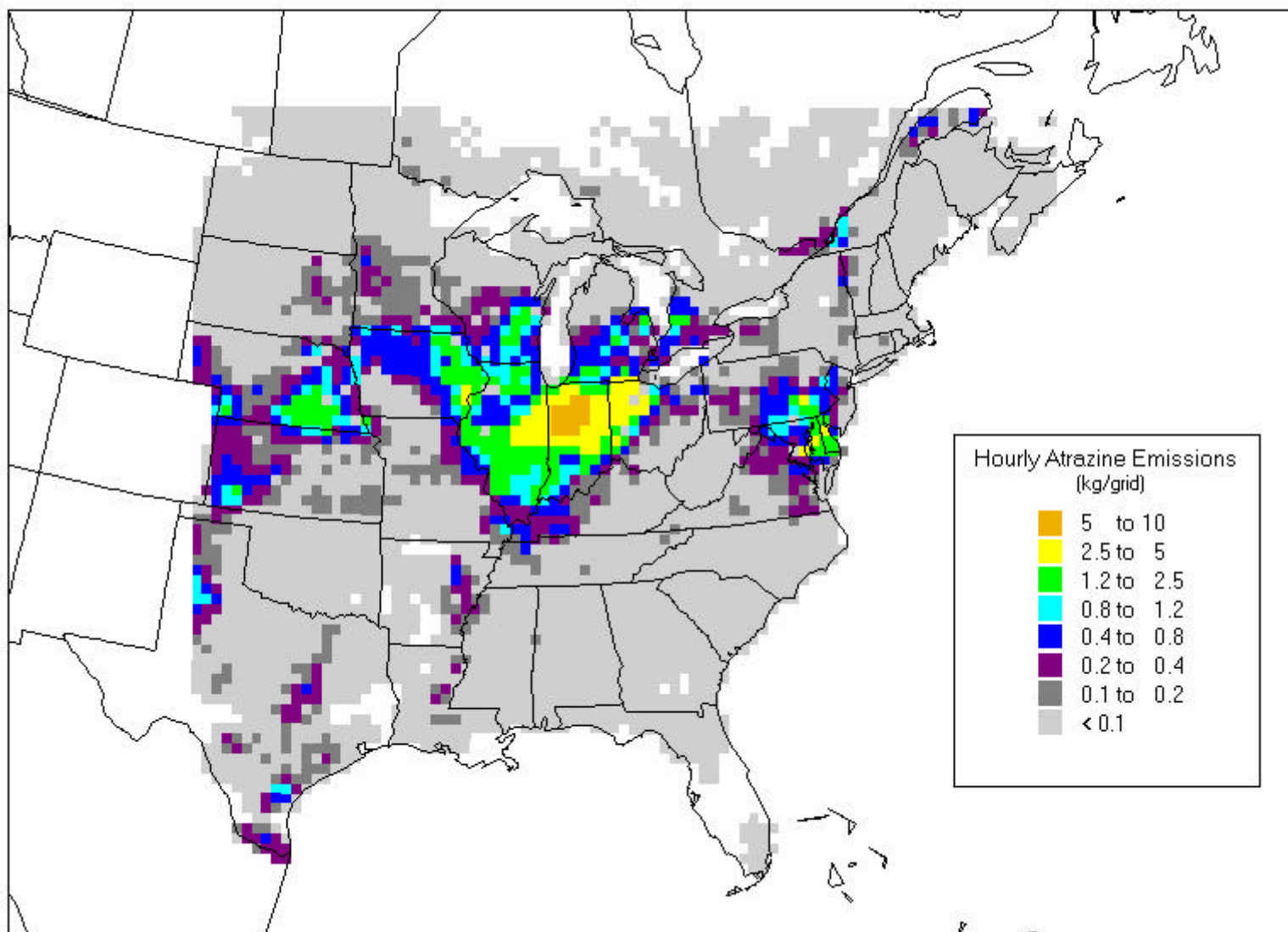


Figure 4.17: Hourly atrazine emissions for Julian day 158 at 14:00 UT (09:00 EST).

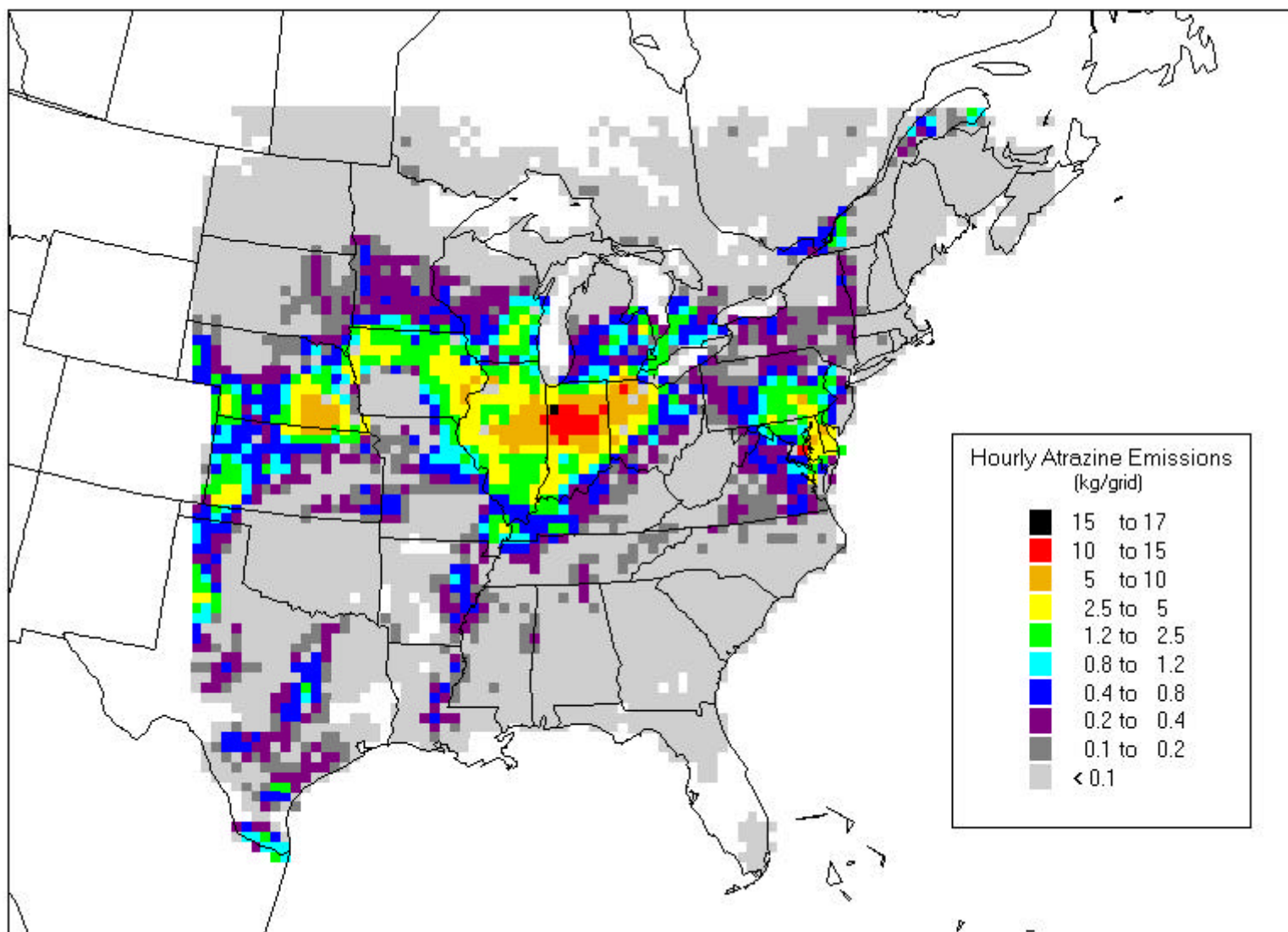


Figure 4.18: Hourly atrazine emissions for Julian day 158 at 19:00 UT (14:00 EST).

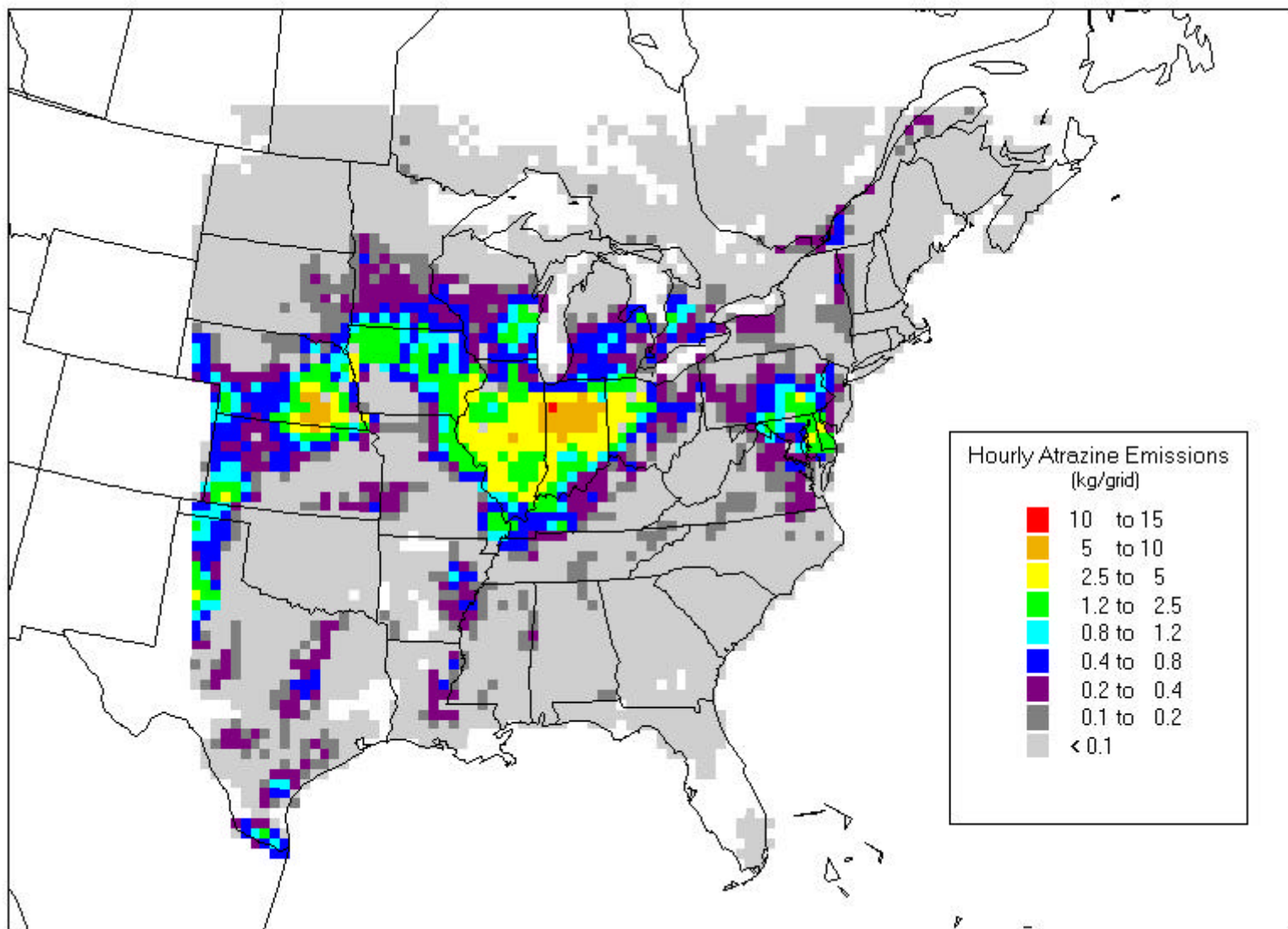


Figure 4.19: Hourly atrazine emissions for Julian day 158 at 24:00 UT (19:00 EST).